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STRONTIOFLUORITE, SrF_2, A NEW MINERAL SPECIES FROM THE KHIBINY MASSIF, KOLA PENINSULA, RUSSIA

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Abstract

Strontiofluorite, SrF_2, is a new member of the fluorite group [cubic, $Fm\bar{3}m$, a 5.713(8) Å, $Z = 4$]. It occurs in a "natrolitized" sodalite – microcline – aegirine lens within apatite-rich urtite at Mt. Koashva in the Khibiny alkaline complex, Kola Peninsula, Russia. The new mineral species is associated with astrophyllite, burbankite, chlorbartonite, fluorapatite, fluorite, lamprophyllite, polezhaevaite-(Ce) and villiaumite. Strontiofluorite occurs as cubo-octahedral crystals (up to 0.5 mm in diameter) and compact masses that cement fibrous aggregates of polezhaevaite-(Ce) in voids caused by leaching of burbankite crystals. Also, strontiofluorite occurs in fine-grained orthoclase-bearing urtite at Mt. Kitchepakhk, also in the Khibiny complex, where it forms lenticular inclusions up to 0.2 mm in length in natrolite and albite associated with orthoclase, nepheline, ferrorichterite, aegirine, lamprophyllite, lorenzenite, stronadelphite and an as-yet unnamed phase of composition Sr_2PO_4F. Strontiofluorite is translucent, pale grey, with a greasy luster and a white streak. Cleavage is perfect on {111}, and the fracture is step-like. The Mohs hardness is 4. In transmitted light, the mineral is colorless, isotropic; $n = 1.438(2)$ (for $\lambda = 589$ nm). The calculated density is 4.11 g cm^{-3}, and the measured density is 4.05 g cm^{-3}. The mean chemical composition of the Koashva sample, determined with an electron microprobe, is (wt.%): Na 1.79, Ca 9.57, Sr 42.81, Ba 7.06, La 2.14, Ce 2.78, Nd 0.64, F 33.15, total 99.94. The empirical formulae calculated on the basis of two atoms of F are: $(Sr_{0.56}Ca_{0.27}Na_{0.09}Ba_{0.06}Ce_{0.02}La_{0.02}Nd_{0.01})_{\Sigma 1.03}F_2$ (Koashva) and $(Sr_{0.88}Ca_{0.08}Na_{0.02}Fe^{2+}_{0.02}Ba_{0.01}Mn_{0.01})_{\Sigma 1.02}F_2$ (Kitchepakhk), which gives a charge imbalance of +0.02. The simplified formula is SrF_2. The strongest lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 3.32(100)(111), 2.886(20)(200), 2.029(90)(220), 1.731(60)(311), 1.317(30)(331) and 1.172(50)(422). The mineral is named as a Sr-dominant analogue of fluorite.

Keywords: strontiofluorite, new mineral species, fluorite group, peralkaline hydrothermal formation, Khibiny complex, Kola Peninsula, Russia.

Sommaire

La strontiofluorite, SrF_2, est un nouveau membre du groupe de la fluorite [cubique, $Fm\bar{3}m$, a 5.713(8) Å, $Z = 4$]. On l'a trouvée dans une lentille de sodalite – microcline – aegyrine partiellement transformée en natrolite au sein de l'urtite riche en apatite au mont Koashva, complexe alcalin de Khibiny, péninsule de Kola, en Russie. Lui sont associés astrophyllite, burbankite, chlorbartonite, fluorapatite, fluorite, lamprophyllite, polezhaevaïte-(Ce) et villiaumite. La strontiofluorite se présente en cristaux cubo-octaédriques atteignant 0.5 mm de diamètre et en masses compactes qui cimentent des agrégats fibreux de polezhaevaïte-(Ce) dans des vacuoles laissées lors du lessivage de cristaux de burbankite. De plus, on a trouvé la strontiofluorite dans un échantillon d'urtite à grains fins porteuse de feldspath potassique au mont Kitchepakhk, complexe de Khibiny, en lentilles de 0.2 mm en longueur incluses dans la natrolite et l'albite associées à orthose, néphéline, ferrorichtérite, aegyrine, lamprophyllite, lorenzenite, stronadelphite, et une phase encore sans nom de composition Sr_2PO_4F. La strontiofluorite est translucide, gris pâle, avec un éclat gras et une rayure blanche. Le clivage {111} est parfait, et la cassure est en paliers. La dureté de Mohs est 4. En lumière transmise, le minéral est incolore, isotrope; $n = 1.438(2)$ (pour $\lambda = 589$ nm). La densité calculée est 4.11 g cm^{-3}, et la densité mesurée est 4.05 g cm^{-3}. La composition moyenne de l'échantillon du mont Koashva, déterminé

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avec une microsonde électronique, est: Na 1.79, Ca 9.57, Sr 42.81, Ba 7.06, La 2.14, Ce 2.78, Nd 0.64, F 33.15, pour un total de 99.94% (poids). Les formules empiriques calculées sur une base de deux atomes de F seraient: $(Sr_{0.56}Ca_{0.27}Na_{0.09}Ba_{0.06}Ce_{0.02}La_{0.02}Nd_{0.01})_{\Sigma 1.03}F_2$ (Koashva) et $(Sr_{0.88}Ca_{0.08}Na_{0.02}Fe^{2+}_{0.02}Ba_{0.01}Mn_{0.01})_{\Sigma 1.02}F_2$ (Kitchepakhk), ce qui donne un écart +0.02 dans le bilan des charges. La formule simplifiée est SrF_2. Les raies les plus intenses du spectre de diffraction X, méthode des poudres [*d* en Å(I)(*hkl*)] sont: 3.32(100)(111), 2.886(20)(200), 2.029(90)(220), 1.731(60)(311), 1.317(30)(331) et 1.172(50)(422). Le nom du minéral indique qu'il s'agit de l'analogue de la fluorite à dominance de Sr.

(Traduit par la Rédaction)

Mots-clés: strontiofluorite, nouvelle espèce minérale, groupe de la fluorite, formation hydrothermale hyperalcaline, complexe de Khibiny, péninsule de Kola, Russie.

INTRODUCTION

The fluoride of strontium, SrF_2, can easily be obtained in a laboratory by reaction between strontium carbonate and hydrofluoric acid: $SrCO_3 + 2HF = SrF_2 + CO_2 + H_2O$. This compound is well studied and used to make, for example, an optical coating on lenses, laser-grade crystals, luminescent spectroscopes, and radio-isotope thermoelectric generators.

In 2008, we found native strontium fluoride in an ultra-agpaitic mineral paragenesis hosted by apatite-rich urtite in the Khibiny alkaline complex in the Kola Peninsula, northwestern Russia. We named this new mineral species *strontiofluorite* to identify it as a Sr-dominant analogue of fluorite. The new mineral and its name were approved by the Commission on New Minerals, Classification and Nomenclature of the International Mineralogical Association (IMA vote 2009–014). The holotype material is housed in the collections of the Mineralogical Museum of St. Petersburg State University and of the Geological and Mineralogical Museum of the Geological Institute, Kola Science Centre, Russian Academy of Sciences in Apatity, Russia (catalogue no. 6455).

OCCURRENCE

Khibiny is the world's largest alkaline complex; it occupies an area of about 1327 km^2 at the current level of erosion. It is located in the western part of the Kola Peninsula, at the contact between the Imandra–Varzuga Proterozoic greenstone belt and Archean metamorphic rocks of the Kola–Norwegian megablock (Fig. 1). The age of the complex is about 380 million years (Kramm & Kogarko 1994). About 70% of its area is occupied by nepheline syenites (foyaites), which are subdivided territorially into two equal parts by a conical intrusion of foidolites known as the Main Ring. Within the Main Ring, rocks of the melteigite – ijolite – urtite series are associated with high-potassium poikilitic nepheline syenite, texturally diverse apatite–nepheline, titanite–nepheline and titanite–apatite rocks, and subordinate volumes of malignite. Pegmatites, which host an unusually large number of mineral species (about 300), are common throughout the Khibiny complex, but are predominantly concentrated in poikilitic nepheline syenites and foidolites of the Main Ring, including several localities at Mt. Koashva in the southeastern part of Khibiny (Yakovenchuk *et al.* 2005).

Strontiofluorite was found in a sodalite – microcline – aegirine – natrolite lens about 3 m in diameter within apatite-rich urtite at Mt. Koashva. We interpret this lens as a product of hydrothermal "natrolitization" of a primary pegmatitic mineral assemblage. The lens has gradational concentric zoning. Its marginal part (up to 0.5 m thick) consists of large (up to 20 cm in maximum dimension) crystals of microcline and aegirine spherulites, with interstitial nepheline and sodalite. Titanite, arfvedsonite and eudialyte (partially replaced by catapleiite) are common also, whereas lamprophyllite and lorenzenite (partially replaced by vinogradovite) are comparatively rare. The central zone (about 2 m in diameter) consists mainly of porous aggregate of natrolite crystals with relict grains of sodalite and fibrous aegirine spherulites up to 20 cm in diameter. Natrolite forms well-shaped crystals (up to 15 cm long) hosting numerous inclusions of fibrous astrophyllite, aegirine and pectolite, platy crystals of leucophanite and tainiolite, well-shaped equant crystals of elpasolite, short prismatic crystals of chlorbartonite, intergrowths of galena, sphalerite and ilmenite, platy crystals of orickite, colloform aggregates of pyrochlore, fine-grained aggregates and well-shaped crystals of fluorapatite, and etched crystals of burbankite (up to 2 cm long). The latest-stage minerals include strontiofluorite–polezhaevaite-(Ce) pseudomorphs after burbankite, druses of small albite crystals in voids, powdery aggregates of fluorite, etched crystals of villiaumite, and solid organic segregations impregnated with tiny inclusions of thorianite.

Strontiofluorite also was found in fine-grained orthoclase- and natrolite-bearing urtite at Mt. Kitchepakhk, close to the southern margin of the Khibiny complex, where it forms pseudomorphs after long prismatic crystals of lamprophyllite (up to 200 μm) in intimate association with aegirine, lorenzenite and an unnamed phase of composition Sr_2PO_4F. Other associated minerals include albite, nepheline, sodalite, pectolite, ferrorichterite, astrophyllite, aenigmatite, eudialyte, rinkite, fluorapatite, stronadelphite, ilmenite, magnetite, fluorite, pyrrhotite and pyrite.

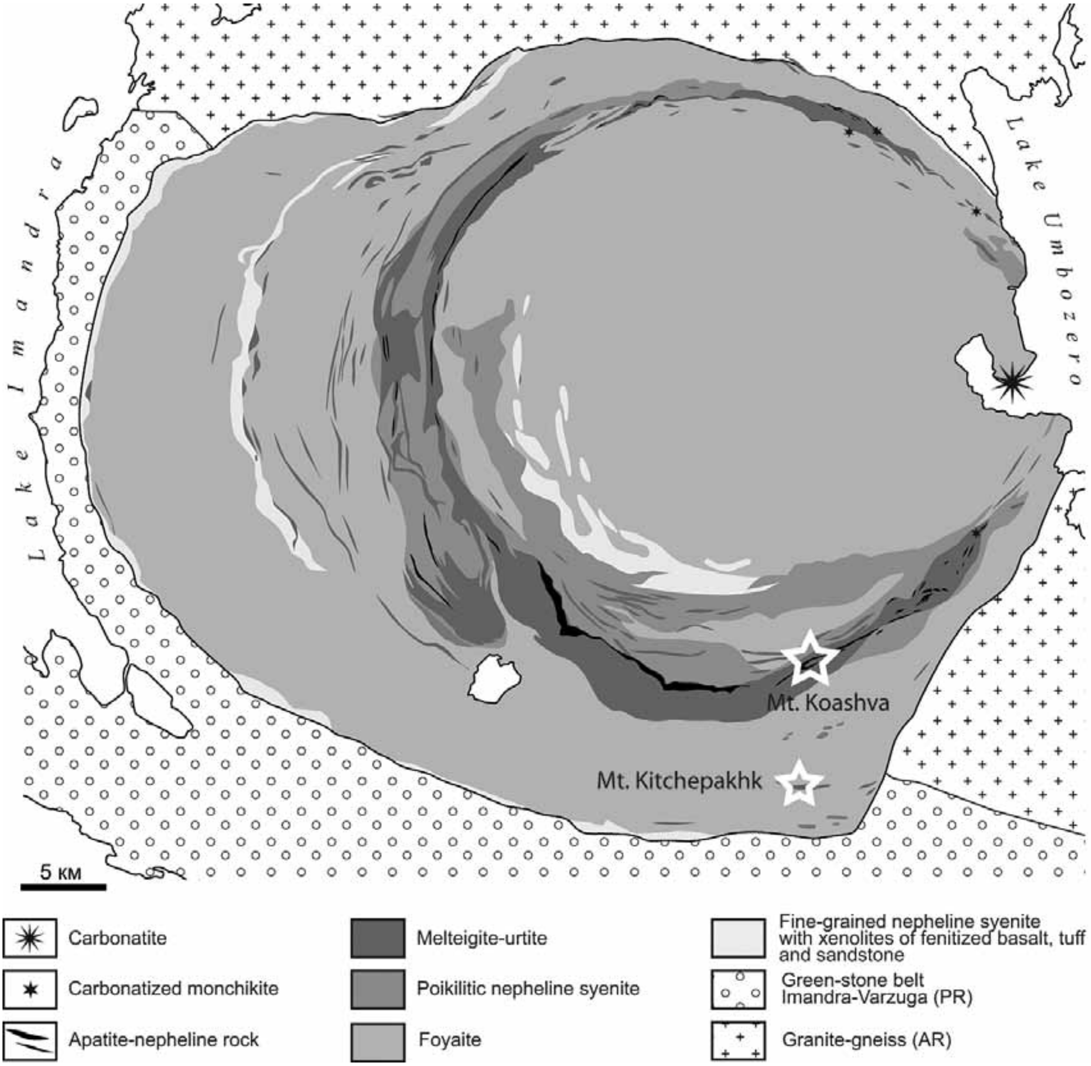

FIG. 1. Simplified geological map of the Khibiny massif (after Snyatkova *et al.* 1983). White stars indicates the strontiofluorite localities.

General Appearance, Physical and Optical Properties

At Mt. Koashva, strontiofluorite forms spherical grains up to 1 mm in diameter and well-shaped cubo-octahedral crystals up to 0.3 mm in diameter, usually penetrated by fibers of polezhaevaite-(Ce) (Yakovenchuk *et al.* 2010), which are confined to voids caused by leaching of burbankite crystals (Fig. 2a). At Mt. Kitchepakhk, minute cubic crystals of strontiofluorite (up to 20 μm in diameter) together with grains of Sr_2PO_4F form partial or complete pseudomorphs after long prismatic crystals of lamprophyllite (Fig. 2b). No twinning was observed. Macroscopically, strontiofluorite is pale gray with a greasy luster. The mineral is translucent, with a white streak and a perfect cleavage on {111}. Strontiofluorite is brittle and has a step-like fracture. The Mohs hardness is 4. The density determined by the sink–float method in Clerici solution is 4.05 g•cm^{-3}, which is in a good agreement with the calculated density of 4.11 g•cm^{-3}. Strontiofluorite is isotropic, with an index of refraction of 1.438(2). In transmitted light, the mineral is colorless and has a high negative relief. A Gladstone–Dale calculation provides a

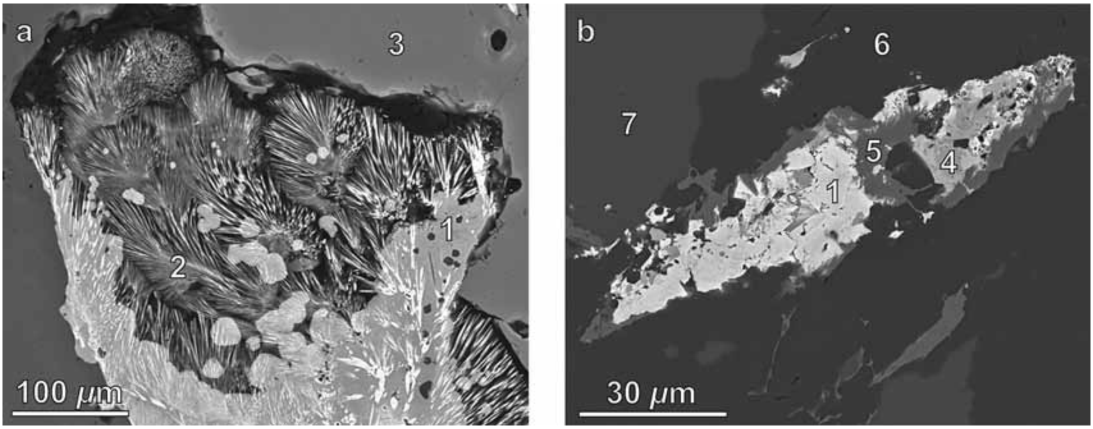

FIG. 2. BSE images showing: (a) strontiofluorite (1) with inclusions of fibrous polezhaevaite-(Ce) (2) in leached burbankite (3) from a "natrolitized" microcline – aegirine – sodalite lens in orthoclase-bearing urtite at Mt. Koashva; (b) pseudomorphs of strontiofluorite (1) and Sr_2PO_4F (4) after lamprophyllite, from natrolite–orthoclase-bearing urtite at Mt. Kitchepakhk. Other associated minerals include aegirine (5), albite (6) and orthoclase (7).

compatibility index of 0.052, which is regarded as good (Mandarino 1981).

CHEMICAL COMPOSITION

The chemical composition of strontiofluorite was studied using a Leo–1450 scanning-electron microscope equipped with a Röntek energy-dispersive spectrometer (for fluorine), as well as a Cameca MS–46 electron microprobe (Geological Institute, Kola Science Centre of the Russian Academy of Sciences, Apatity) operated in wavelength-dispersive mode at 20 kV and 15 nA, with a beam diameter of 10 μm (for cations). The following standards were used: lorenzenite (Na), wollastonite (Ca), celestine (Sr), barite (Ba), synthetic $LaCeS_2$ (La and Ce), synthetic $LiNd(MoO_4)_2$ (Nd), and fluorite (F). Table 1 provides mean analytical results (where each composition is the average of 6–10 point measurements) for four different crystals of strontiofluorite from Mt. Koashva and one grain from Mt. Kitchepakhk. The empirical formulae of the mineral (calculated on the basis of two F atoms) are: $(Sr_{0.56}Ca_{0.27}Na_{0.09}Ba_{0.06}Ce_{0.02}La_{0.02}Nd_{0.01})_{\Sigma 1.03}F_2$ (Mt. Koashva) and $(Sr_{0.88}Ca_{0.08}Na_{0.02}Fe^{2+}_{0.02}Ba_{0.01}Mn_{0.01})_{\Sigma 1.02}F_2$ (Mt. Kitchepakhk), which gives a charge imbalance of +0.02. The generalized simplified formula of strontiofluorite is SrF_2.

TABLE 1. CHEMICAL COMPOSITION OF STRONTIOFLUORITE

	Mt. Koashva				Mt. Kitchepakhk
	Mean	Minimum	Maximum	Std. dev.	
Na wt.%	1.79	1.23	2.43	0.63	0.38
Ca	9.57	8.10	11.36	1.36	2.68
Mn	n.d.	n.d.	n.d.		0.46
Fe	n.d.	n.d.	n.d.		0.93
Sr	42.81	39.28	47.67	4.15	62.96
Ba	7.06	4.83	8.79	1.94	1.15
La	2.14	n.d.	4.88	2.52	0.33
Ce	2.78	n.d.	6.16	3.24	0.46
Nd	0.64	n.d.	1.27	0.73	n.d.
F	33.15	32.88	33.71	0.36	31.00
Total	99.94				100.35

POWDER X-RAY-DIFFRACTION PATTERN

The powder X-ray-diffraction pattern of strontiofluorite was obtained with a URS–1 instrument equipped with a 114.7-mm Debye–Scherrer camera and Fe*K*α X-ray source, operated at 40 kV and 30 mA (Table 2). The unit-cell parameter of the Koashva sample, determined from the powder pattern, is 5.713(8) Å, and the cell volume is 186.5(3) Å^3 ($Z = 4$). According to Youngman & Smith (2008), this parameter increases linearly from 5.463 for pure CaF_2 to 5.78 Å for pure SrF_2, following the relationship a (Å) = $5.463 + 0.317x_{Sr}$. The measured unit-cell parameter is intermediate between the end-member values and insignificantly larger than the calculated parameter (5.640 Å). The small discrepancy is evidently due to presence of large cations at the (Sr,Ca) site. Thus, strontiofluorite is a Sr-dominant analogue of fluorite and a natural analogue of synthetic SrF_2 (Table 3).

DISCUSSION

Strontium is a common substituent element in fluorite from the Khibiny complex; its content ranges from 0.1 wt.% (0.001 Sr atoms per formula unit, *apfu*) in most pegmatites to 18 wt.% (0.18 *apfu*) in a fenitized volcanogenic–sedimentary rock (authors' unpubl. data). The Ca content of strontiofluorite ranges from 0.1 to 0.3 *apfu*, *i.e.*, the fluorite–strontiofluorite series appears to exhibit a gap between $Ca_{0.7}Sr_{0.3}F_2$ and $Ca_{0.4}Sr_{0.6}F_2$ (Fig. 3). The existence of a complete series of intermediate compositions between CaF_2 and SrF_2 has been well established experimentally (*e.g.*, Youngman & Smith 2008), implying that the apparent miscibility-gap and non-linearity of the Ca–Sr relationship can be caused by a geochemical reason. Indeed, the end members of this series are virtually free of substituent elements such as rare-earth elements (REE), *etc*. The intermediate compositions, in contrast, contain significant levels of Na and REE in accordance with the heterovalent substitution $2(Ca, Sr)^{2+} \leftrightarrow Na^+ + REE^{3+}$, which culminates with the formation of polezhaevaite-(Ce) (Fig. 4). If the incorporation of Na, REE and Ba in these fluoride minerals is taken into account, there is an excellent correlation between the content of divalent cations and that of (Na + REE).

The solubility of SrF_2 in water is eight times greater than solubility of CaF_2, and hydrothermal fluorite usually accommodates an appreciable amount of Sr. However, in the hydrothermally affected pegmatite at Koashva, strontiofluorite crystallizes *in situ* as a result of the alteration of burbankite by a F-rich hydrothermal fluid:

$$\underset{\text{burbankite}}{Na_3(Sr_{1-x}Ca_x)_2Ce(CO_3)_5} + 10(HF)_{aq}$$
$$= \underset{\text{polezhaevaite-(Ce)}}{NaSrCeF_6} + \underset{\text{strontiofluorite}}{(1-x)SrF_2}$$
$$+ \underset{\text{fluorite}}{xCaF_2} + \underset{\text{villiaumite}}{2NaF} + 5(CO_2)_{aq} + 5H_2O.$$

Polezhaevaite-(Ce) is the first mineral to appear in this sequence, and strontiofluorite cements fibers of polezhaevaite-(Ce). The latest minerals are villiaumite and fluorite. In some cases, polezhaevaite–strontiofluorite intergrowths are coated with a thin crust of secondary

TABLE 2. POWDER-DIFFRACTION DATA FOR STRONTIOFLUORITE AND SYNTHETIC SrF_2 AND CaF_2

	Strontiofluorite Mt. Koashva			Synthetic SrF_2 ICDD 06-0262		Synthetic CaF_2 ICDD 35-0816	
hkl	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}	d_{obs} (Å)
111	100	3.324	3.321	100	3.352	92	3.1546
200	20	2.886	2.876	25	2.900	<1	2.731
220	90	2.029	2.034	80	2.0508	100	1.931
311	60	1.731	1.734	50	1.7486	33	1.647
222	10	1.654	1.660	6	1.6743	1	1.577
400	20	1.434	1.438	16	1.4499	10	1.365
331	30	1.317	1.320	20	1.3303	9	1.253
420				10	1.2966	1	1.221
422	50	1.172	1.174	25	1.1840	17	1.115
511	20	1.105	1.107	16	1.1164		

TABLE 3. COMPARISON OF STRONTIOFLUORITE, SYNTHETIC SrF_2 AND FLUORITE

	Strontiofluorite, SrF_2 this work	Synthetic SrF_2 ICDD 06-0262	Fluorite, CaF_2 Anthony *et al.* (1997)
Crystal system	Cubic	Cubic	Cubic
Space group	*Fm*$\bar{3}$*m*	*Fm*$\bar{3}$*m*	*Fm*$\bar{3}$*m*
a, Å	5.713	5.800	5.463
Z	4	4	4
Strongest lines in powder pattern	3.32(100), 2.886(20), 2.029(90), 1.731(60), 1.317(30), 1.172(50)	3.352(100), 2.900(25), 2.051(80), 1.748(50), 1.330 (20), 1.184(25)	1.931 (100), 3.153 (94), 1.647 (35), 1.1150 (16), 1.366 (12), 1.253 (10)
Density, g cm^{-3}	4.05 (meas.)	4.276 (calc.)	3.175–3.184 (meas.)
Mohs hardness	4	4	4
Color	Pale grey	Colorless	Various colors or colorless
Optical character	Isotropic	Isotropic	Isotropic
n	1.438	1.438	1.434
Habit of crystals	Cubo-octahedral		Cubo-octahedral
Cleavage	Perfect along {111}		Perfect along {111}

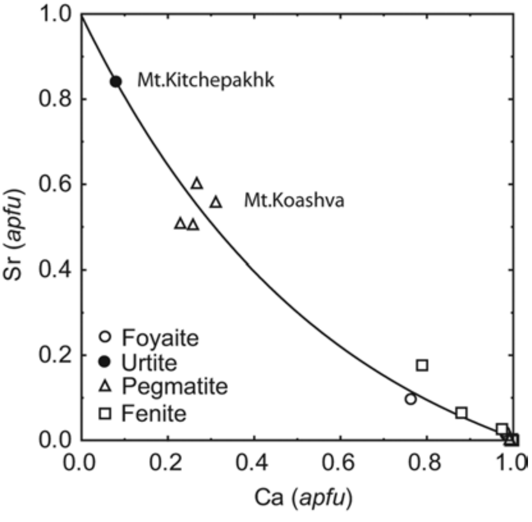

FIG. 3. Variation of Sr *versus* Ca content in fluorite and strontiofluorite from the Khibiny complex.

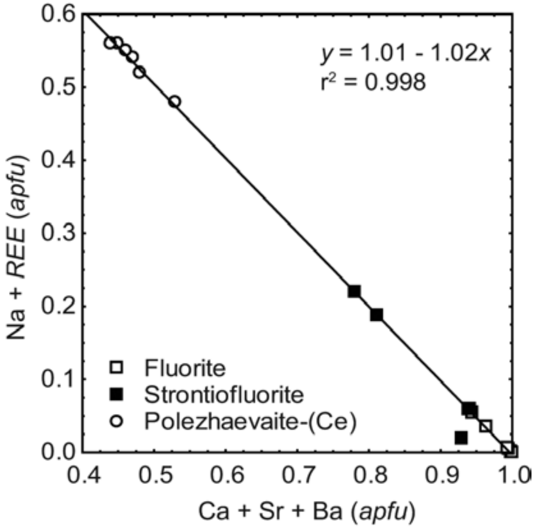

FIG. 4. Content of divalent cations *versus* Na + REE in fluorite, strontiofluorite and polezhaevaite-(Ce) from the Khibiny complex.

burbankite that was formed when the F content in the fluid decreased owing to the above reaction, and residual cations reacted with dissolved CO_2.

In the feldspar-bearing urtite at Kitchepakhk, both strontiofluorite and Sr_2PO_4F are products of the alteration of lamprophyllite by hydrothermal fluids enriched in F and PO_4:

$$2\underset{\text{lamprophyllite}}{Sr_2Na_3Ti_3Si_4O_{17}(OH)} + 5(HF)_{aq} + (H_3PO_4)_{aq} = 2\underset{\text{strontiofluorite}}{SrF_2} + Sr_2PO_4F + 3\underset{\text{lorenzenite}}{Na_2Ti_2Si_2O_9} + 2(SiO_2)_{aq} + 5H_2O.$$

Therefore, we can conclude that strontiofluorite is a characteristic secondary mineral produced by intense alteration of primary Sr-bearing minerals by F-rich hydrothermal fluids in peralkaline parageneses.

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