American Mineralogist, Volume 95, pages 1080–1083, 2010

Polezhaevaite-(Ce), $NaSrCeF_6$, a new mineral from the Khibiny massif (Kola Peninsula, Russia)

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ABSTRACT

Polezhaevaite-(Ce) $NaSrCeF_6$ is a new member of the gagarinite mineral group [hexagonal, $P6_3/m$, $a = 6.207(7)$ Å, $c = 3.801(9)$ Å, $V = 126.8(2)$ Å^3, $Z = 1$]. It is found in a natrolitized microcline-aegirine-sodalite lens within apatite-rich urtite at Mt. Koashva (Khibiny massif, Kola Peninsula, Russia) in association with aegirine, albite, arfvedsonite, astrophyllite, burbankite, catapleiite, chlorbartonite, djerfisherite, elpasolite, fluorapatite, fluorite, galena, hydroxylapatite, ilmenite, lamprophyllite, lorenzenite, leucophanite, microcline, natrolite, nepheline, orickite, pectolite, pyrochlore, sodalite, sphalerite, strontiofluorite, tainiolite, titanite, vinogradovite, and villiaumite. Polezhaevaite-(Ce) occurs as parallel and sheaf-like aggregates of extremely thin fibers (up to 1 mm long and <1 µm thick), which fill leaching voids within burbankite crystals in natrolite and mantles around partially dissolved burbankite crystals in intimate association with strontiofluorite. Polezhaevaite-(Ce) is translucent (transparent in separate fibers), snowy-white, with a silky luster (in aggregates) and a white streak. Cleavage is not observed; fracture is splintery (in aggregates). The Mohs hardness of individual crystals could not be determined and approaches 3 in aggregates. In transmitted light, the mineral is colorless, uniaxial positive: $\varepsilon = 1.497(5)$, $\omega = 1.490(5)$ (for $\lambda = 589$ nm). $D_{calc} = 4.646$ g/cm^3, $D_{meas} = >4.2$ g/cm^{-3}. The mean chemical composition determined by electron microprobe is (wt%): Na 5.27, Ca 3.08, Sr 29.72, Ba 0.48, La 11.76, Ce 14.12, Pr 0.49, Nd 3.09, F 31.95, total 99.96. Empirical formula calculated on the basis of F = 6 apfu is: $(Na_{0.82}Ca_{0.18})_{\Sigma=1.00}(Sr_{1.21}Ce_{0.36}La_{0.30}Ca_{0.09}Nd_{0.08}Ba_{0.01})_{\Sigma=2.06}F_6$ (charge imbalance is +0.05). Its simplified formula is $NaSrCeF_6$. The strongest X-ray powder-diffraction lines [*d* in Å, (*I*), (*hkl*)] are: 5.416(40)(100), 3.120(100)(101, 110), 2.198(70)(201), 1.796(90)(121, 211, 300, 102), 1.554(30)(220), 1.173(70)(321, 231, 140, 410,132, 312, 113). The mineral is named in honor of Lyudmila Ivanovna Polezhaeva (b. 1935), a Russian expert in electron microprobe analysis of minerals for her contribution to the mineralogy of alkaline rocks.

Keywords: Polezhaevaite-(Ce), new mineral, gagarinite group, peralkaline hydrothermal formation, Khibiny massif, Kola Peninsula, Russia

INTRODUCTION

The Khibiny massif in Kola Peninsula (Russia) is the largest alkaline intrusion in the world, occupying an area of 1327 km^2 at the current erosion level. It was emplaced at the contact between the Imandra-Varzuga Proterozoic greenstone belt and Archaean metamorphic complexes of the Kola-Norwegian megablock. About 70% of its area is underlain by nepheline syenites (foyaite) of monotonous modal composition that, in most works, are subdivided into two units of comparable size, proper foyaite (in the center) and "khibinite" (peripheral with respect to the foyaite), separated from each other by the so-called Central Ring complex (Yakovenchuk et al. 2005). The Central Ring complex is composed predominantly of foidolites (melteigite-ijolite-urtite), highly potassic (leucite-normative) poikilitic nepheline syenite (rischorrite), and less common malignite, as well as subordinate amounts of titanite-nepheline, titanite-apatite, and apatite-nepheline rocks. Pegmatite and hydrothermal veins, characterized by unusually diversified mineralogy (about 300 mineral species), are common throughout the massif, but mostly concentrated within rischorrite and foidolites of the Central Ring. In the last 10 years, most new mineral discoveries have been made in the Koashva apatite-nepheline deposit, which has been exploited to a depth of 600 m by open-cast methods. In this mine, foidolitic rocks below the ore body contain numerous ultra-agpaitic hydrothermal bulb-shaped bodies up to 5 m in diameter. These "bulbs" consist of microcline, nepheline, sodalite, natrolite, aegirine, villiaumite, and a variety of rare minerals formed by hydrothermal alteration of peralkaline pegmatites.

The Sr-Ce analog of gagarinite-(Y) and the closely associated new species strontiofluorite were discovered by the authors in 2008 in one of the natrolitized peralkaline pegmatites in apatite-rich urtite. The former mineral was named polezhaevaite-(Ce) in honor of Lyudmila Ivanovna Polezhaeva (b. 1935), an expert in electron microprobe analysis of minerals from the Geological Institute of the Kola Science Center of the Russian Academy of Sciences (Apatity, Russia) for her contribution to the mineralogy

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0003-004X/10/0007–1080$05.00/DOI: 10.2138/am.2010.3361

of alkaline rocks, which included the discovery of crawfordite, gmelinite-K, kostylevite, lintisite, mineevite-(Y), nabaphite, paranatisite, paraumbite, sazykinaite-(Y), shkatulkalite, shomiokite-(Y), sitinakite, and umbite.

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA, no. 2009-015). The holotype material is deposited at the Mineralogical Museum of the Geological Institute of the Kola Science Center (no. 6454) and in the Mineralogical Museum of St. Petersburg State University (St. Petersburg, Russia).

OCCURRENCE

Polezhaevaite-(Ce) was found in a natrolitized microcline-aegirine-sodalite lens about 3 m in diameter in apatite-rich urtite at Mt. Koashva. The marginal zone of this lens is up to 0.5 m thick and consists of large (up to 20 cm in length) microcline crystals and aegirine spherulites, with interstitial nepheline and sodalite. Titanite, arfvedsonite, and eudialyte (partially replaced by catapleiite) are also common, whereas lamprophyllite and lorenzenite (partially replaced by vinogradovite) are rare. The central zone (about 2 m in diameter) mainly consists of porous natrolite aggregate with relict grains of sodalite and spherulites of fibrous aegirine up to 20 cm in diameter. Natrolite forms well-shaped crystals up to 15 cm in length hosting numerous inclusions of acicular astrophyllite, aegirine and pectolite, platy crystals of leucophanite and tainiolite, well-shaped crystals of elpasolite and 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 corroded crystals of burbankite up to 2 cm in length partially or completely replaced by aggregates of polezhaevaite-(Ce) and strontiofluorite. In these aggregates, fibrous crystals of polezhaevaite-(Ce) are cemented by strontiofluorite in much the same fashion as sand grains are cemented by gypsum in “desert roses.” The latest minerals to crystallize are druses of small (up to 1 mm across) crystals of albite, fluorite, and villiaumite lining voids and associated with solid organic spherules (up to 2 mm across) with thorianite inclusions.

GENERAL APPEARANCE, PHYSICAL AND OPTICAL PROPERTIES

Polezhaevaite-(Ce) occurs as parallel and sheaf-like aggregates of extremely thin fibers (up to 1 mm in length and <1 μm in thickness), confined to dissolution voids within burbankite crystals hosted by natrolite (Fig. 1a) and mantles around partially dissolved burbankite crystals, and is intimately associated with strontiofluorite (Fig. 1b). Twinning is not observed. Macroscopically, aggregates of polezhaevaite-(Ce) are snowy-white with a silky luster. The mineral is translucent to opaque (in aggregates), with a white streak. Cleavage is not observed. Polezhaevaite-(Ce) is ductile (separate fibers are elastic) and has a splintery fracture. The Mohs hardness of individual crystals could not be tested, and approaches 3 in aggregates. The calculated density of polezhaevaite-(Ce) is 4.646 g/cm^3, and measured density is >4.2 g/cm^3 (the mineral sinks slowly in a concentrated Clerici solution). The mineral is unixial positive: $\varepsilon = 1.497(5)$, $\omega = 1.490(5)$ (for $\lambda = 589$ nm). In transmitted light, the mineral is colorless and lacks pleochroism and dispersion. The Gladstone-Dale constant (Mandarino 1981) is 0.045 (good).

CHEMICAL COMPOSITION

The chemical composition of polezhaevaite-(Ce) was determined using a Leo-1450 scanning electron microscope with a Röntek EDS system (used for fluorine analysis) and a Cameca MS-46 electron microprobe (Geological Institute, Apatity) operated in wavelength-dispersion mode at 20 kV, 10 nA, with a beam diameter of 5 μm (used for cations). The following standards were used: fluorite (F), lorenzenite (Na), wollastonite (Ca), celestine (Sr), barite (Ba), and synthetic $LaCeS_2$ (La and Ce), $LiPr(WO_4)_2$ (Pr), and $LiNd(MoO_4)_2$ (Nd). Table 1 provides mean analytical results for seven different aggregates of polezhaevaite-(Ce) (each analysis is the average analysis of 6–10 points). The empirical formula calculated on the basis of

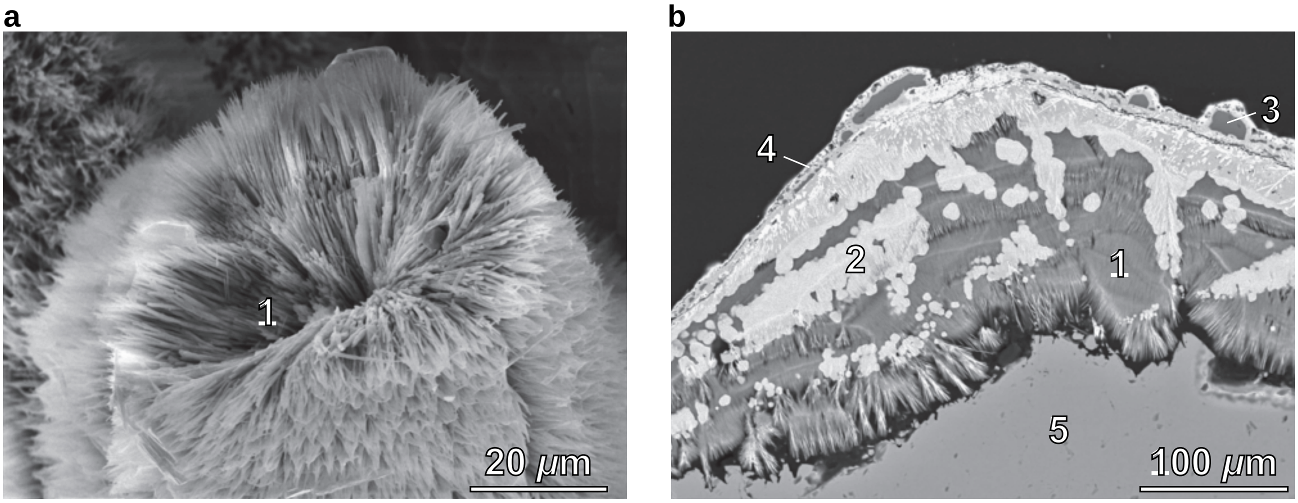

FIGURE 1. Secondary electron (**a**) and back-scattered electron (**b**) images showing fibrous aggregates of polezhaevaite-(Ce) (1) cemented by strontiofluorite (2) and coated by fluorite (3) and secondary burbankite (4), which are developed in partially dissolved crystals of primary burbankite (5) from a natrolitized microcline-aegirine-sodalite lens in apatite-rich urtite, Mt. Koashva, Khibiny, Kola.

6 F atoms per formula unit (apfu) is $(Na_{0.82}Ca_{0.18})_{\Sigma=1.00}(Sr_{1.21}Ce_{0.36}La_{0.30}Ca_{0.09}Nd_{0.08}Ba_{0.01})_{\Sigma=2.06}F_6$, which gives a charge imbalance of +0.05, and the simplified formula can be written as $NaSrCeF_6$. In all of the studied samples, the Sr content exceeds the REE content; the principal substitution mechanism is: $^{[A]}Na^+ + {}^{[B]}REE^{3+} \leftrightarrow {}^{[A]}Ca^{2+} + {}^{[B]}Sr^{2+}$.

The Ce:La ratio in polezhaevaite-(Ce) is variable, but is always greater than 1 in the central part of a spherulite and, in some spherulites, decreases to less than 1 in the marginal zone, which can be regarded as "polezhaevaite-(La)."

TABLE 1. Chemical composition of polezhaevaite-(Ce), wt%

Constituent	Mean	Minimum	Maximum	Std. dev.
Na	5.27	2.54	7.45	1.80
Ca	3.08	2.21	7.08	1.77
Sr	29.72	28.56	31.08	0.92
Ba	0.48	0.00	1.16	0.60
La	11.76	7.49	14.24	2.47
Ce	14.12	11.42	17.13	1.78
Pr	0.49	0.00	1.19	0.62
Nd	3.09	1.14	6.48	1.87
F	31.95	31.15	32.70	0.55
Total	99.96			

TABLE 2. X-ray powder diffraction data for polezhaevaite-(Ce) and gagarinite-(Y)

Polezhaevaite-(Ce)				Gagarinite-(Y) (Stepanov and Severov 1961)		
I	D_{obs}	D_{calc}	*hkl*	*I*	D_{obs}	*hkl*
40	5.416	5.375	100	30	5.24	100
100	3.120	3.104	101, 110	50	3.00	110
				50	2.92	101
10	2.684	2.688	200	10	2.60	200
10	2.409	2.404	111	20	2.28	111
70	2.198	2.195	201	90	2.086	201
20	2.032	2.032	210, 120	20	1.962	210
10	1.905	1.901	002	20	1.763	002
90	1.796	1.792	121, 211, 300, 102	100	1.717	211
				10	1.668	102
20	1.619	1.621	112, 301	20	1.518	112
30	1.554	1.552	220, 202	20	1.498	220
				10	1.460	202
				20	1.435	310
30	1.387	1.388	311, 131, 212, 122	20	1.334	311
				10	1.315	212
				10	1.297	400
30	1.304	1.304	302		1.237	302
10	1.267	1.267	401	10	1.218	401
				10	1.191	320
10	1.201	1.202	222	10	1.143	222
70	1.173	1.173	321, 231, 140, 410, 132, 312, 113	30	1.129	321
				10	1.115	312

X-RAY POWDER DIFFRACTION DATA

X-ray powder diffraction (XRD) data for polezhaevaite-(Ce) were obtained using an URS-1 instrument equipped with a 114.7 mm Debye-Scherrer camera and Fe$K\alpha$ source and operated at 40 kV and 30 mA (Table 2). The XRD pattern can be indexed in a primitive hexagonal unit cell analogous to that of gagarinite-(Y) $NaCaYF_6$, space group $P6_3/m$ (Hughes and Drexler 1994; Frank-Kamenetskaya et al. 1994; Jambor et al. 1996). The unit-cell parameters refined from the XRD data are: a = 6.207(7) Å, c = 3.801(9) Å, V = 126.8(2) Å^3, Z = 1. The measured pattern is in good agreement with the one calculated using the atomic arrangement of gagarinite-(Y) as a structural model (Table 2). As can be expected from the compositional differences between polezhaevaite-(Ce) and gagarinite-(Y), the latter mineral has a much smaller unit cell (Table 3). Both these minerals are chemically and structurally related to zajacite-(Ce) $NaCaCeF_6$, whose XRD pattern, however, shows superlattice reflections indicative of a larger cell (Jambor et al. 1996). The structural and physical characteristics of all three minerals are compared in Table 3. Topologically, these fluorides represent stuffed derivatives from the UCl_3 structure type (Hughes et al. 1994; Jambor et al. 1996). Unfortunately, the habit of polezhaevaite-(Ce) is not amenable to its study by single-crystal methods.

DISCUSSION

Strontium is a common substituent element in fluorite from the Khibiny massif, ranging from nil to 0.2 apfu in abundance. In the new mineral strontiofluorite, the Ca content ranges from 0.1 to 0.3 apfu. In the fluorite-strontiofluorite series, near-end-member compositions are virtually devoid of impurities, whereas intermediate compositions commonly contain Na and REE in accord with the coupled substitution $2(Ca, Sr)^{2+} \leftrightarrow Na^+ + REE^{3+}$, which culminates with the formation of polezhaevaite-(Ce). Obviously, the total content of Na and REE in strontiofluorite and polezhaevaite-(Ce) correlates linearly with that of divalent cations, but the linear trend shows a gap between $(Sr,Ca,Ba)_{0.55}(Na,REE)_{0.45}F_2$ and $(Sr,Ca,Ba)_{0.75}(Na,REE)_{0.25}F_2$ (Fig. 2). This gap is undoubtedly caused by the structural differ-

TABLE 3. Comparison of polezhaevaite-(Ce), gagarinite-(Y), and zajacite-(Ce)

Mineral	Polezhaevaite-(Ce) $Na(SrCe)F_6$	Gagarinite-(Y) $Na(CaY)F_6$	Zajacite-(Ce) $Na(CaCe)F_6$
References	This work	Stepanov and Severov (1961)	Jambor et al. (1996)
Crystal system	Hexagonal	Hexagonal	Trigonal
Space group	$P6_3/m$	$P6_3/m$	$P\bar{3}$
a (Å)	6.21	5.99	6.10
c (Å)	3.80	3.53	11.06
Z	1	1	3
Strongest XRD lines	5.42(40), 3.12(100), 2.198(70), 1.796(90), 1.554(30), 1.173(70)	5.24(30), 3.00(50), 2.92(50), 2.086(90), 1.717(100), 1.129(30)	5.29(70), 3.036(100), 2.146(70), 1.757(80), 1.152(40), 0.9189(40)
Density (g/cm^3)	4.65 (calc)	4.21 (meas)	4.44 (meas)
Mohs hardness	ca. 3 (in aggregates)	4.5	3.5
Color	White (in aggregates)	Creamy	Colorless
Opt. character	Uniaxial (+)	Uniaxial or biaxial (+)	Uniaxial (+)
ε	1.497	1.492	1.503
ω	1.490	1.472	1.483
$2V$ (°)	0	0–20	0
Habit	Elongate on c (fibers)	Elongate on c (prismatic)	Anhedral grains
Cleavage	None observed	{100} distinct	None observed

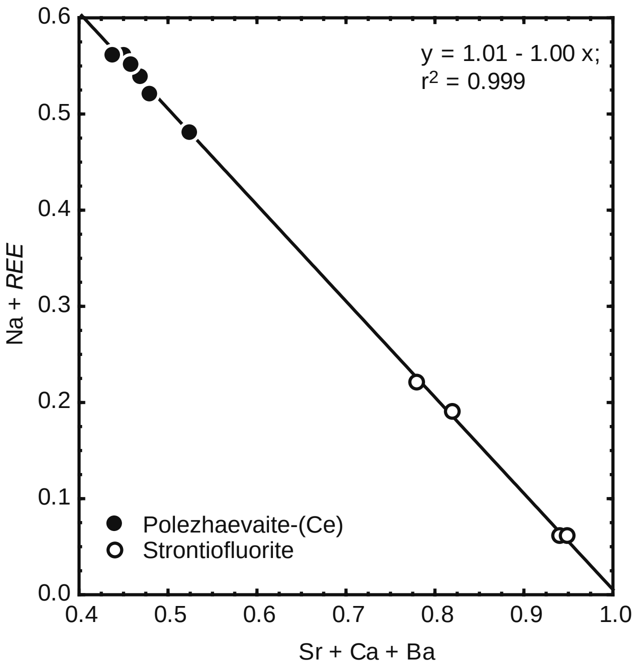

FIGURE 2. Variation in the total content of divalent cations relative to the Na+REE content (expressed as apfu to a total of one cation) in coexisting polezhaevaite-(Ce) and strontiofluorite from Mt. Koashva, Khibiny, Kola.

ences between (strontio)fluorite and polezhaevaite-(Ce).

Formation of polezhaevaite-(Ce) and strontiofluorite at the expense of burbankite involves alteration of the latter mineral by fluorine-rich low-temperature hydrothermal fluids:

$$Na_3(Sr_{1-x}Ca_x)_2Ce(CO_3)_5 + 10(HF)_{aq} =$$
$$NaSrCeF_6 + (1-x)SrF_2 + xCaF_2 + 2NaF + 5(CO_2)_{aq} + 5H_2O.$$

Polezhaevaite-(Ce) is the earliest mineral to crystallize in this assemblage, and strontiofluorite precipitates when the bulk of REE is bound in polezhaevaite-(Ce). The latest minerals to form are fluorite and villiaumite. In some cases, intergrowths of polezhaevaite-(Ce) and strontiofluorite are covered with a thin crust of secondary burbankite (Fig. 1b), which formed when the fluid became depleted in F^- anions due to the above reaction, and residual cations combined with dissolved CO_2.

The primary burbankite contains about 6 wt% CaO, and Ca is a common substituent in both polezhaevaite-(Ce) and strontiofluorite. Given that the total content of Sr and REE in the unit cell of polezhaevaite-(Ce) is close to 2.0, we assume that Ca substitutes for Na in the interstitial A site to compensate for the excess Sr in the B site (see above): ${}^{[A]}Na^+ + {}^{[B]}REE^{3+} \leftrightarrow {}^{[A]}Ca^{2+} + {}^{[B]}Sr^{2+}$. If this conjecture is correct, Sr is the dominant cation in the B site and the name polezhaevaite should not be followed by a Levinson modifier (Levinson 1966). However, CNMNC IMA recommended that the name polezhaevaite-(Ce) be used instead as it is in better accord with the existing nomenclature of Na-rare-earth fluorides. The name will need to be revised if a REE-dominant counterpart of polezhaevaite is discovered. Given that one atom of Na per unit cell is the maximum occupancy of the interstitial A site in this type of structure (e.g., Hughes et al. 1994), such compositions (i.e., $Na_{1-x}REE_{1+x}Sr_{1-x}F_6$) may exist.

ACKNOWLEDGMENTS

We thank the Swiss National Foundation for financial support (Project IB 7320-110675). Our fieldwork was funded by the Apatit Joint Stock Company and Laplandia Minerals Ltd. Also, we are grateful to Igor Pekov and an anonymous referee for many constructive comments on the manuscript, and Anton Chakhmouradian for his editorial help.

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MANUSCRIPT RECEIVED JULY 31, 2009
MANUSCRIPT ACCEPTED FEBRUARY 28, 2010
MANUSCRIPT HANDLED BY ANTON CHAKHMOURADIAN