Stronadelphite, Sr₅(PO₄)₃F, a new apatite-group mineral

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Abstract: The new apatite-group mineral stronadelphite was found in the Belovitovove peralkaline pegmatite at the Kirovskii apatite mine, Mt. Kukisvumchorr, Khibiny alkaline complex, Kola peninsula, Russia. Associated minerals are natrolite, microcline, aegirine, pectolite, lamprophyllite, belovite-(Ce), belovite-(La), gaidonnayite, nenadkevichite, komarovite, manganokukisvumite, epididymite, sphalerite, neotocite, etc. Stronadelphite forms hexagonal, prismatic to acicular crystals up to $0.1 \times 0.1 \times 2$ mm, combined in sheaf-like clusters up to 1×2 mm embedded in natrolite. The mineral is transparent, colourless with a pale greenish tint. Stronadelphite is brittle, with Mohs hardness 5, no cleavage observed. D_{calc} is 3.915 g/cm³. Optically, the new mineral is uniaxial (-), ω 1.630(1), ε 1.623(1). Average values for six point microprobe analyses (wt%) are: Na₂O 0.10, CaO 2.49, SrO 62.72, BaO 2.40, La₂O₃ 0.34, Ce₂O₃ 0.22, ThO₂ 0.28, P₂O₅ 29.02, F 1.45, H₂O(calc.) 0.54, -O=F₂ - 0.61; total 98.95. The empirical formula based on 13 anions $[O_{12}(F,OH)]$ is: $(Sr_{4.46}Ca_{0.33}Ba_{0.12}Na_{0.02}La_{0.02}Ce_{0.01}Th_{0.01})_{\Sigma=4.97}P_{3.01}O_{12}[F_{0.56}(OH)_{0.44}]_{\Sigma=1}$. The idealized formula is $Sr_5(PO_4)_3F$. Stronadelphite is hexagonal, space group $P6_3/m$; a = 9.845(7), c = 7.383(4) Å, V = 619.7(7) Å³, Z = 2. Its crystal structure has been refined to R = 0.0305 using single-crystal X-ray diffraction data. Stronadelphite is isostructural with fluorapatite. The strongest lines of the powder diffraction pattern [d in Å (I) (hkl)] are: 3.71 (30) (002), 3.21 (40) (120, 210), 2.940 (100) (211, 121, 112), 2.823 (35) (300, 202), 2.009 (50) (222, 312, 132), 1.955 (45) (213, 123), 1.500 (30) (151, 511, 332). The mineral is named after the chemical element strontium and $\alpha\delta\epsilon\lambda\phi\delta\sigma$, Greek for "brother", as the full strontium analogue of fluorapatite, the most widespread member of the apatite supergroup. Both the mineral and its name have been approved by the IMA CNMNC. The type specimen is deposited in Fersman Mineralogical Museum, Moscow, with the registration number 3693/1.

Key-words: stronadelphite, new mineral, apatite group, crystal structure, peralkaline pegmatite, Khibiny alkaline complex, Kola peninsula, strontium flurophosphate.

1. Introduction

Phosphate minerals of the apatite supergroup possess strong affinity for strontium. Sr^{2+} is the most typical cation substituting for Ca^{2+} in fluorapatite, $Ca_5(PO_4)_3F$, and hydroxylapatite, Ca₅(PO₄)₃OH. In alkaline and, especially, peralkaline complexes of igneous rocks, apatite-like phosphates with species-defining Sr also occur: there are belovite-(Ce), NaCeSr₃(PO₄)₃F, belovite-(La), NaLaSr₃ (PO₄)₃F, fluorstrophite (formerly "strontium-apatite"), SrCaSr₃(PO₄)₃F, fluorcaphite, SrCaCa₃(PO₄)₃F, and deloneite, (Na_{0.5}*REE*_{0.25}Ca_{0.25}) (Ca_{0.75}*REE*_{0.25})Sr_{1.5}(CaNa_{0.25}) $REE_{0.25}$)(PO₄)₃F_{0.5}(OH)_{0.5}. All these minerals are cationordered: Sr is significantly (or even almost completely, as in case of belovites) dominating at one or two structural sites; this results in the lowering of symmetry from $P6_3/m$ (the space group of the apatite archetype structure) to $P6_3$ (fluorstrophite, fluorcaphite), $P\overline{3}$ (belovites), or P3 (deloneite) (Pasero et al., 2010).

In this paper we describe the Sr-richest apatite-supergroup mineral with the idealized formula $Sr_5(PO_4)_3F$. It is named stronadelphite (Cyrillic: стронадельфит) after the chemical element *stron*tium and αδελφόσ, Greek for "brother": the mineral is the full strontium end-member analogue of fluorapatite, the most widespread species of the apatite supergroup. The mineral was accepted as a new species by the IMA CNMNC in 2008 (IMA no. 2008-009) but approval of its name was suspended until the elaboration and acceptance of a new nomenclature system for the apatite supergroup proposed by an *ad-hoc* CNMNC subcommittee. The full description of this new mineral was approved in 2010 in the frame of this nomenclature (Pasero *et al.*, 2010).

It is worth noting that a mineral chemically close to stronadelphite was first found by one of us (SNB) in a peralkaline pegmatite at Mt. Karnasurt, Lovozero alkaline complex, Kola Peninsula, Russia, and briefly reported as "strontium-apatite", with quantitative chemical data, by Pekov (2000). This sample, consisting of curved platy crystals, was unsuitable for single-crystal X-ray study but its belonging to the apatite group was clearly confirmed by powder X-ray diffraction data. Later, a single electronmicroprobe analysis of a mineral with apatite-type stoichiometry and similar chemical composition was published by Chakhmouradian *et al.* (2002): it was found as μ m-sized individuals in chemically highly variable, thin rims surrounding fluorapatite crystals in a peralkaline pegmatite at Mt. Alluaiv in the same Lovozero complex.

The material described in the present paper was collected in the neighbouring Khibiny alkaline complex by the amateur mineral collector A.S. Podlesnyi, who gave it to us for studies. This has to be considered the holotype stronadelphite. Only one thumbnail-size specimen, containing several crystal clusters of the new mineral, was found. On the basis of the chemical data (Table 1), we believe that also the above-mentioned material from Lovozero corresponds to stronadelphite.

Table 1. Chemical composition of stronadelphite.

	1	2	3
Constituent		wt%	
Na ₂ O	0.10 (0.06-0.12)	n.d.	0.21
CaO	2.49 (2.4-2.6)	4.8-7.2	2.59
SrO	62.72 (62.4-62.9)	61.3-63.9	62.86
BaO	2.40 (1.9-2.6)	0.5-1.6	n.d.
PbO	n.d.	0.0-0.4	
La_2O_3	0.34 (0.2-0.4)	n.d.	0.74
Ce_2O_3	0.22 (0.0-0.3)	n.d.	0.71
Nd_2O_3	n.d.	n.d.	0.23
ThO ₂	0.28 (0.2-0.6)	n.d.	
SiO ₂	n.d.	n.d.	0.39
P_2O_5	29.02 (28.7-29.6)	28.1-29.5	27.86
F	1.45 (1.3–1.5)	3.32	2.42
H ₂ O(calc.)	0.54		0.05
$-O=F_2$	-0.61	-1.40	-1.02
Total	98.95	100.0-100.8	97.04
	Formula calculate	d on the basis of 13	anions with

Formula calculated on the basis of 13 amons with $O_{12}(F,OH)$

Na	0.02		0.05
Ca	0.33	0.63-0.89	0.35
Sr	4.46	4.26-4.38	4.55
Ba	0.12	0.02-0.07	
Pb		0.00-0.01	
La	0.02		0.03
Ce	0.01		0.03
Nd			0.01
Th	0.01		
Si			0.05
Р	3.02	2.87-2.93	2.95
F	0.56	1.21-1.29	0.96
OH	0.44		0.04
0	12.00	11.71–11.79	12.00

n.d. - not detected.

1 –Belovitovoye pegmatite, Kirovskii mine, Khibiny (the holotype, our data: averaged for 6 point analyses, range is given in parentheses); 2 – Mt. Karnasurt, Lovozero (our data, F was determined separately by the ion-selective method); 3 – Mt. Alluaiv, Lovozero (Chakhmouradian *et al.*, 2002: reported as "strontium-apatite"). The type specimen of stronadelphite is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, with the registration no. 3693/1.

2. Occurrence

Stronadelphite was found in the Belovitovoye pegmatite uncovered by underground mine working on the level +252 m of the Kirovskii apatite mine at Mt. Kukisvumchorr, in the southern part of the Khibiny alkaline complex, Kola peninsula, Russia. This pegmatite, which represents the type locality also for belovite-(La) (Pekov *et al.*, 1996) and nechelyustovite (Nèmeth *et al.*, 2009), was described in detail by Pekov & Podlesnyi (2004) and is shortly outlined here.

The Belovitovoye peralkaline pegmatite is a sinuous and branched vein cross-cutting inequigranular nepheline syenite with accessory eudialyte and rinkite. Its thickness varies from 3 cm to 0.5 m. In pinches the vein has no zoning and consists of potassic feldspar, pyroxene of the aegirine-diopside series, nepheline, eudialyte, and lamprophyllite. The zoning is observed in bulges: the selvages have the abovementioned mineral composition, the intermediate zone consists of aggregates of white coarse-crystalline microcline and the core is composed by colourless blocky natrolite. In some areas, a thin rim of columnar pectolite is observed between the microcline and natrolite zones.

The natrolite nests, formed as a result of hydrothermal alteration of earlier hyperagpaitic assemblage, contain variable mineralization. Aegirine, belovite-(Ce), belovite-(La), stronadelphite, nechelyustovite, sphalerite, galena and molybdenite are embedded in natrolite, together with pseudomorphs of several types: Na-rich komarovite after vuonnemite, gaidonnayite after eudialyte, and neotocite after a pectolite-sérandite series mineral. Late minerals are also represented by nenadkevichite, Na-depleted komarovite, manganokukisvumite, epidydimite, apophyllite-(F), ancylite-(Ce), pyrite, CO₃-bearing hydroxylapatite, and an unidentified clay mineral which typically occur in fractures or small cavities.

3. General appearance and physical properties

Stronadelphite forms hexagonal, prismatic to acicular crystals up to 2 mm long and 0.1 mm thick, combined in sheaf-like clusters up to 1×2 mm (Fig. 1). They occur in massive or cavernous natrolite and are typically intimately intergrown with a clay mineral. The main form of stronadelphite crystals is a hexagonal prism, probably {10-10}, termination faces are {0001}.

The new mineral is transparent, nearly colourless with a pale greenish tint. Streak is white. Lustre is vitreous. Stronadelphite shows cream-coloured fluorescence in shortwave (254 nm) UV radiation and does not fluoresce under long-wave UV radiation. The mineral is brittle, and its Mohs hardness is five. Cleavage was not observed, fracture is uneven. Density was not measured because of the small size of unpolluted individual grains; $D_{calc} = 3.915 \text{ g/cm}^3$.



Fig. 1. Sheaf-like cluster of acicular crystals of stronadelphite in natrolite (the holotype specimen) from the Belovitovoye pegmatite, Kirovskii mine, Khibiny. Field of view width is 4 mm. Photo: I.V. Pekov & A.V. Kasatkin.

Optically, stronadelphite is uniaxial negative, with $\omega = 1.630(1)$ and $\varepsilon = 1.623(1)$. Under the microscope, it is colourless and nonpleochroic.

4. Chemical data

The electron-microprobe study of stronadelphite was carried out on a Camebax SX 50 microanalyser using wavelength-dispersive spectroscopic (WDS) mode, an operating voltage of 15 kV, a beam-current of 30 nA and a beam diameter 3 μ m. The standards used were: albite (Na), fluorapatite (Ca, P, F), SrSO₄ (Sr), BaSO₄ (Ba), LaPO₄ (La), CePO₄ (Ce), and ThO₂ (Th). Contents of K, Pb, Y, lanthanides heavier than Ce, U, Mn, Fe, Al, Si, S, As, V, and Cl were below their detection limits. H₂O and CO₂ contents were not measured directly because of scarcity of material. Chemical composition of the mineral is given in Table 1.

The empirical formula of stronadelphite based on 13 total anions, with the anionic part of formula established as $O_{12}(F,OH)$, following Pasero *et al.* (2010), is (Sr_{4.46} Ca_{0.33}Ba_{0.12}Na_{0.02}La_{0.02}Ce_{0.01}Th_{0.01}) Σ =4.97P_{3.01}O₁₂ [F_{0.56} (OH)_{0.44}] Σ =1. The idealized formula is Sr₅(PO₄)₃F, which requires SrO 69.83, P₂O₅ 28.69, F 2.56, -O=F₂ -1.08, total 100.00 wt%.

The Gladstone-Dale compatibility index calculated from the empirical formula and $D_{\text{calc}} = -0.024$ (excellent).

5. X-ray crystallography and crystal-structure refinement

The X-ray powder pattern of stronadelphite (Table 2) was obtained using a 114.6 mm diameter Debye-Scherrer camera, with Ni-filtered CuK α -radiation. The unit-cell dimensions refined from the powder data are: a = 9.879(3), c = 7.378(4) Å, V = 623.6(7) Å³, Z = 2.

A single crystal was used for the intensity data collection that was carried out on a conventional four-circle Ital Structures diffractometer. The crystallographic features, the details of the X-ray diffraction study and the structure refinement are given in Table 3. An empirical absorption correction was applied on the basis of ψ -scan measurements. The structure was refined in the space group $P6_3/m$ using SHELXL-97 program package (Sheldrick, 2008). Trials to lower the symmetry to $P6_3$ did not result in any improvement of the structural model, and were eventually neglected. The final positional and displacement parameters in the structure of stronadelphite (Fig. 2a) are given in Table 4.

6. Discussion

Stronadelphite is a member of the apatite group, a subdivision of the apatite supergroup (Pasero *et al.*, 2010). The new mineral and fluorapatite are isostructural. The synthetic analogue of stronadelphite, $Sr_5(PO_4)_3F$ (Swafford & Holt, 2002; Yuan *et al.*, 2007; Sghir *et al.*, 2009), as well as synthetic $Sr_5(PO_4)_3OH$ (Sudarsanan & Young, 1972) and $Sr_5(PO_4)_3Cl$ (Sudarsanan & Young, 1980), adopt the same structure type.

In the fluorapatite structure ($P6_3/m$), Ca cations occupy two independent sites with different coordination numbers: nine-fold-coordinated *M*1 sites and seven-fold-coordinated *M*2 sites (Hughes & Rakovan, 2002). Thus, the crystal-chemical formula of fluorapatite is ^{IX}[Ca]₂^{VII} [Ca]₃(PO₄)₃F. Its Sr-analogue stronadelphite has the idealized end-member formula ^{IX}[Sr]₂^{VII}[Sr]₃(PO₄)₃F.

The synthetic compounds $Ca_5(PO_4)_3F$ and $Sr_5(PO_4)_3F$ form a continuous solid-solution series (Akhavan-Niaki, 1961; Sghir *et al.*, 2009). Numerous analyses of apatitegroup minerals, both reported in many publications and performed by us, show that the same behaviour is displayed also by their natural analogues. However, the intermediate part of this natural series is complicated by cation ordering [like, *e.g.*, in the well-known calcite CaCO₃ – dolomite CaMg(CO₃)₂ – magnesite MgCO₃ series] (for details see Pan & Fleet, 2002). All published structural data for natural intermediate members of the Ca₅(PO₄)₃F solid-solution series, at first fluorcaphite and fluorstrophite, display Ca-Sr ordering.

A structural study of the type specimen of "strontiumapatite", a mineral recently renamed fluorstrophite (Pasero *et al.*, 2010) from the Inagli alkaline complex, Yakutia, Russia, was carried out by Klevtsova (1964) in the space group *P*6₃. In this structure (Fig. 2b), the four *M*1 sites, equivalent in space group *P*6₃/*m*, transform into two pairs of sites *M*1 and *M*1'. The *M*1 site is occupied by Ca and the *M*1' site is occupied by Sr and minor Ba resulting in the disappearance of the mirror plane and the centre of symmetry; in the *M*2 site Sr prevails over Ca (Fig. 3). The crystalchemical formula of the type specimen of fluorstophite is $^{M1}[(Sr,Ba)]^{M1'}[Ca]^{M2}[Sr_{2.05}Ca_{0.30}A_{0.15}](PO_4)_3(F,OH) where$ *A*=*REE*, Na,*etc.*(Klevtsova, 1964). A similar result was

I _{meas}	$d_{\rm meas}$, Å	I _{calc}	$d_{ m calc}$, Å	hkl
5	5.60	1	5.587	101
20	4.19	27, 8	4.278, 4.105	200, 111
30	3.71	32	3.701	002
15	3.29	43	3.388	102
40	3.21	9, 35	3.234, 3.234	120, 210
100	2.940	100, 48, 99	2.962, 2.962, 2.956	211, 121, 112
35	2.823	74, 12	2.852, 2.794	300, 202
5	2.569	2	2.470	220
5	2.398	12	2.373	130
10	2.317	2	2.342	221
5	2.225	14	2.202	113
10	2.154	4, 4	2.139, 2.132	400, 203
50	2.009	41, 7, 21	2.052, 1.996, 1.996	222, 312, 132
45	1.955	31, 15	1.958, 1.958	213, 123
20	1.918	10, 17	1.897, 1.897	231, 321
15	1.852	9, 17	1.867, 1.867	410, 140
50	1.831	31, 20	1.850, 1.845	402,004
5	1.743	1, 2, 1	1.733, 1.733, 1.728	232, 322, 114
5	1.683	2, 3	1.694, 1.666	204, 412
5	1.628	1, 1, 6	1.647, 1.617, 1.617	330, 420, 240
20	1.561	11, 12	1.552, 1.549	502, 304
10	1.518	3, 1, 9	1.537, 1.534, 1.534	510, 233, 323
30	1.500	2, 8, 7	1.504, 1.504, 1.504	151, 511, 332
5	1.471	1, 0.5, 0.5, 0.5, 0.5	1.487, 1.481, 1.478, 1.456, 1.456	413, 422, 224, 134, 314
10	1.315	5, 1, 2, 4, 10	1.330, 1.314, 1.314, 1.312, 1.312	602, 432, 342, 414, 144
15	1.285	2, 2, 9	1.285, 1.284, 1.284	611, 522, 252

Table 2. X-ray powder-diffraction data of stronadelphite.

Table 3. Crystal data, data collection information and refinement details for stronadelphite.

Crystal system, space group	Hexagonal, P6 ₃ /m
Unit-cell dimensions	a = 9.845(7), c = 7.383(4) Å
Volume	$619.7(7) \text{ Å}^3$
Ζ	2
Radiation and wavelength	MoKα; 0.71069 Å
Temperature	293(2) K
Index ranges	$0 \le h \le 10, -10 \le k \le 8, -7$
-	$\leq l \leq 6$
Reflections collected	761
Independent reflections	$160 (R_{int} = 0.0811)$
with $I > 2\sigma(I)$	
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	42
$R(F)_{obs} [I > 2\sigma(I)]$	0.0305
$R_{\rm W}({\rm F}^2)$ [$I > 2\sigma({\rm I})$]	0.0709
<i>R</i> indices (all data)	$R(F) = 0.0314$, w $R(F^2) = 0.0724$
Largest diff. peak and hole	0.87 and $-0.92 \ e/\text{\AA}^3$



Fig. 2. Crystal structures of stronadelphite (**a**: this work) and fluorstrophite (**b**: Klevtsova, 1964). PO₄ groups are shown as tetrahedra, alkaline-earth cations and F anions as circles.

reported for "strontium-apatite" from Mt. Rasvumchorr, Khibiny. The same space group $P6_3$ and the same character of cation arrangement were found: M1 [Sr_{0.75} Ca_{0.25}] ${}^{M1'}$ [Ca_{0.7} Sr_{0.3}] M2 [Sr_{2.6}Ca_{0.4}](PO₄)₃F (Pushcharovsky *et al.*, 1987). Thus, the generalized crystal-chemical formula of fluorstrophite is IX [Sr,Ca] IX [Ca,Sr] VII [Sr,Ca]₃(PO₄)₃F (Table 5).

Fluorcaphite, a mineral with gross dominance of Ca over Sr, has the same space group $P6_3$ and generally the same type of cation order as fluorstrophite but, differing from the

latter, the *M*2 site in it is Ca-dominant (Fig. 3). The crystalchemical formula of the type specimen of fluorcaphite is M1 [Sr_{0.5}Na_{0.3}Ca_{0.2}] ${}^{M1'}$ [Ca] M2 [Ca_{2.1}Sr_{0.6}*REE*_{0.3}](PO₄)₃ [F_{0.7}(OH)_{0.3}] (Rastsvetaeva & Khomyakov, 1996). The generalized crystal-chemical formula of fluorcaphite is IX [Sr,Na,Ca] IX [Ca] VII [Ca,Sr,*REE*]₃(PO₄)₃(F,OH). Its simplified formula is (SrCa)Ca₃(PO₄)₃F. Space group *P*6₃ and ordering of cations at the *M*1, *M*1' and *M*2 sites were

Atom	x	у	Z	$U_{ m eq}$	
$\overline{M1} = \operatorname{Sr}_{0.9}\operatorname{Ca}_{0.1}$	0.3333	0.6667	-0.0004(4)	0.0206(13)	
M2 = Sr	0.2393(2)	-0.0147(2)	0.25	0.0208(10)	
Р	0.4005(6)	0.3689(6)	0.25	0.0165(17)	
01	0.3326(14)	0.4826(13)	0.25	0.018(3)	
02	0.5804(14)	0.4640(15)	0.25	0.028(4)	
03	0.3455(13)	0.2637(11)	0.0797(14)	0.028(3)	
F	0.0	0.0	0.25	0.074(13)	

Table 4. Fractional atomic coordinates and equivalent displacement parameters ($Å^2$) for stronadelphite.



Fig. 3. Idealized schemes of the cation arrangement in fluorapatite (**a**: Hughes & Rakovan, 2002), stronadelphite (**b**: this work), fluorstrophite (**c**: Klevtsova, 1964), and fluorcaphite (**d**: Rastsvetaeva & Khomyakov, 1996). Ca-dominant sites are shown as yellow circles, Sr-dominant sites as green circles; m – mirror planes in the structures with space group $P6_3/m$.

reported by Chakhmouradian *et al.* (2005) for fluorcaphitelike phases from Khibiny and Lovozero differing in cation composition and arrangement.

Thus, all published structural data for natural intermediate (*i.e.*, with significant contents of both Ca and Sr) members of the Ca₅(PO₄)₃F – Sr₅(PO₄)₃F solid-solution series indicate cation ordering and the space group $P6_3$. In contrast, fluorapatite and stronadelphite, *i.e.*, minerals with compositions close to the end-members of the series, do not show such cation order (no sufficient amounts of different cations for ordering) and, correspondingly, adopt the holosymmetric space group $P6_3/m$. These two isostructural minerals are characterized by the predominance of the same cation – Ca or Sr, respectively – in all cation sites (Table 5, Fig. 3).

The U_{eq} value of the X site is rather large (Table 4), undoubtedly as a result of significant substitution of F by OH. Such value indicates possible displacement of the anion from Wyckoff position 2a (0, 0, 0.25) towards position 4e (0, 0, z) typical for OH-dominant apatites. However the attempts to "move" or split the X position were not successful.

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Table 5.	Comparati	ive data	for the natura	l members	of the	$Ca_5(PC)$	$(D_4)_3 F$	– Sr ₅ (F	$PO_4)_3F$	⁷ solid-solutio	n series
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Mineral	Fluorapatite	Fluorcaphite	Fluorstrophite	Stronadelphite	
Formula	$Ca_5(PO_4)_3F$	$(SrCa)Ca_3(PO_4)_3F$	$(SrCa)Sr_3(PO_4)_3F$	$Sr_5(PO_4)_3F$	
formula	$^{11}Ca_2 ^{11}Ca_3 (PO_4)_3F$	$Sr^{11}Ca^{11}Ca_3 (PO_4)_3F$	$^{11}\text{Sr}^{11}\text{Ca}^{11}\text{Sr}_3 (PO_4)_3\text{F}$	$(PO_4)_3F$	
Space group	$P6_3/m$	<i>P</i> 6 ₃	$P6_3$	$P6_3/m$	
a, Å	9.35-9.38	9.485	9.57-9.63	9.845	
<i>c</i> , Å	6.86-6.89	7.000	7.12-7.22	7.383	
Density, g/cm ³	3.18	3.60	3.84	3.92	
References	Hughes & Rakovan (2002)	Rastsvetaeva & Khomyakov (1996)	Klevtsova (1964); Pushcharovsky <i>et al.</i> (1987)	this work	

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