

## Fluorcalciobriitholite, (Ca,REE)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>F, a new mineral: description and crystal chemistry

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**Abstract:** The new mineral fluorcalciobriitholite, ideally Ca<sub>3</sub>Ce<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)F, has been found at Mount Kukisvumchorr, Khibiny alkaline complex, Kola Peninsula, Russia, in veinlets which contains aggregates of orthoclase, nepheline, sodalite and biotite in association with grains of fayalite, gadolinite-(Ce), zircon, monazite-(Ce), zirconolite (“polymignite”), fluorapatite, fluorite, molybdenite, löllingite and graphite. Fluorcalciobriitholite forms long-prismatic hexagonal crystals up to 0.5 x 10 mm; the main crystal form is the hexagonal prism {10-10}. The mineral is transparent, with a pale pinkish to brown colour and a white streak. The hardness (Mohs) is 5.5, and the observed density is 4.2(1) g/cm<sup>3</sup>. Optically, it is uniaxial (-) with ω 1.735(5), ε 1.730(5). Electron microprobe gave the following empirical formula based on [Si+P+S] = 3 *apfu*: [Ca<sub>2.80</sub> (Ce<sub>0.93</sub>La<sub>0.54</sub>Nd<sub>0.26</sub>Y<sub>0.18</sub>Pr<sub>0.08</sub>Sm<sub>0.03</sub>Gd<sub>0.03</sub>Dy<sub>0.02</sub>Yb<sub>0.02</sub>Er<sub>0.01</sub>)<sub>Σ2.12</sub> Th<sub>0.04</sub>Mn<sub>0.03</sub> Sr<sub>0.02</sub>]<sub>Σ4.99</sub> [(Si<sub>1.94</sub>P<sub>1.06</sub>)<sub>Σ3</sub>O<sub>12</sub>] [F<sub>0.76</sub>O<sub>0.22</sub>Cl<sub>0.01</sub>]<sub>Σ0.99</sub> (Z = 2). The IR spectrum of metamict fluorcalciobriitholite from Siberia showed a marked similarity with those of hydroxylbriitholite-(Ce) and hydroxylbriitholite-(Y). The strongest lines of the X-ray powder pattern [*d* in Å (*I*) (*hkl*)] are: 3.51 (45) 002, 3.15 (70) 102, 2.85 (100) 211, 121, 2.78 (60) 300. The mineral is hexagonal, space group *P6<sub>3</sub>/m*, with *a* = 9.580(7), *c* = 6.985(4) Å, *V* = 555.2(7) Å<sup>3</sup>. The crystal structure was refined from single-crystal X-ray diffraction data to *R<sub>F</sub>* = 0.029. Fluorcalciobriitholite, whose simplified formula is (Ca,REE)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>F, differs from fluorbriitholite in having Ca > ΣREE, and differs from fluorapatite in having Si > P. Its compositional field falls within the limits Ca<sub>2.5</sub>REE<sub>2.5</sub>(SiO<sub>4</sub>)<sub>2.5</sub>(PO<sub>4</sub>)<sub>0.5</sub>F (boundary with fluorbriitholite) and Ca<sub>3.5</sub>REE<sub>1.5</sub>(SiO<sub>4</sub>)<sub>1.5</sub>(PO<sub>4</sub>)<sub>1.5</sub>F (boundary with fluorapatite). Both the mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names.

**Key-words:** fluorcalciobriitholite, new mineral, crystal structure, Khibiny alkaline complex, briitholite group, apatite group.

### Introduction

Briitholites are silicates (typically phosphorus-bearing) with apatite-type structure and the general formula (REE,Ca)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>X, where REE include yttrium, as usual, and X = (OH)<sup>-</sup>, F<sup>-</sup>, or Cl<sup>-</sup>. So far hydroxylbriitholite-(Ce), (Ce,Ca)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>(OH) (synonyms: beckelite, lessingite, pravdite), hydroxylbriitholite-(Y)\*, (Y,Ca)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>(OH)

(formerly abukumalite), and fluorbriitholite-(Ce), (Ce,Ca)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>F are considered as valid mineral species (Winther, 1901; Hata, 1938; Levinson, 1966; Gu *et al.*, 1994). Briitholites are hexagonal with space group *P6<sub>3</sub>/m* or *P6<sub>3</sub>*, or monoclinic pseudo-hexagonal with space group *P2<sub>1</sub>* (Gay, 1957; Li *et al.*, 1981; Kalsbeek *et al.*, 1990; Genkina *et al.*, 1991; Zhang *et al.*, 1992; Noe *et al.*, 1993; Gu *et al.*, 1994; Oberti *et al.*, 2001). Usually these minerals contain significant impurities (thorium, and sometimes also uranium), with consequent metamictization which make them completely or partially amorphous to X-rays.

Briitholites are widespread in alkaline rocks, especially in pegmatites and metasomatites related to syenite and nepheline-syenite complexes. In some of the alkaline complexes

\* We are aware that in the mineralogical literature (see, for instance, Gaines *et al.*, 1997) these minerals are referred to as briitholite-(Ce) and briitholite-(Y). In this paper, however, we will make use, whenever possible, of specifying prefixes (*e.g.*, fluor-, or hydroxyl-), in view of a likely official revision of the nomenclature of briitholites, as it was already done for apatites.

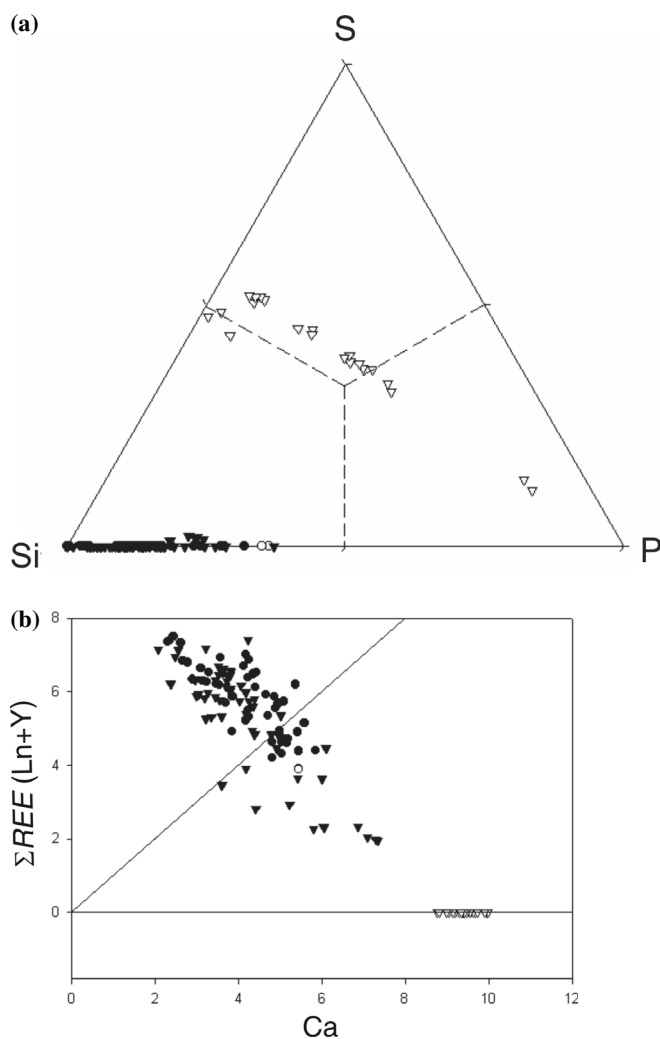


Fig. 1. (a) P:Si:S ratios in minerals of the britholite and ellestadite groups. (b) Ca:ΣREE ratios in minerals of the britholite and ellestadite groups. S- and Si-enriched apatite has been also included. Circles = our data; triangles = earlier published data. Empty circles show range of composition of the holotype specimen of fluorcalciobriholite from Khibiny; empty triangles show composition of minerals of the apatite – ellestadite solid solution system with significant contents of Si and S. Earlier published analyses for britholite-group minerals were taken from the following summarizing publications (Kupriyanova *et al.*, 1966; Vasil'eva, 1978; Nekrasova & Nekrasov, 1980; Lazarenko *et al.*, 1981; Kapustin, 1986), and also from some recent papers (Kalsbeek *et al.*, 1990; Gu *et al.*, 1994; Jamtveit *et al.*, 1997; Oberti *et al.*, 2001). Earlier published analyses for ellestadite-group minerals were taken from Rouse & Dunn (1982) and Chesnokov *et al.* (1987).

significant deposits, also commercially important, of REE and Th with members of the series hydroxylbritholite-(Ce) – fluorbritholite-(Ce) as major ore minerals are known (Solodov *et al.*, 1991).

The history of studies on britholites dates back to the beginning of the last century (Winther, 1901) and resulted in almost one hundred published chemical analyses, both wet and electron microprobe. Most of them point to the above-reported formula. However at least a dozen analyses of “britholite”

correspond to a different chemical formula,  $(Ca,REE)_5[(Si,P)O_4]_3X$ , which differs from the preceding one in having  $Ca > \Sigma REE$

A systematic and comprehensive study of 35 samples of “britholite” from 19 localities of Russia, Ukraine, Kazakhstan, Kyrgyzstan, Norway, Greenland, Canada, USA, and Korea confirms that the minerals with  $\Sigma REE > Ca$  are by far more common in nature, even if members with  $Ca > \Sigma REE$  are not so rare. The latter can not be considered as proper rare-earth minerals, in accordance with the accepted nomenclature (Bayliss & Levinson, 1988), at difference from britholites *sensu stricto*. On the other hand they can not be identified as apatites, in which it is  $P > Si$ .

Thus, there exist a family of minerals with a specific composition field: apatite-like P-bearing silicates with Ca prevailing over  $\Sigma REE$ . They form a continuous solid-solution series with “true”, namely REE-dominant, britholites (Fig. 1), but not with apatites. It seems correct to propose the generic name calciobriholite for these minerals, adding for each mineral species a prefix which reflects the prevailing X anion.

Britholites can be considered either a subgroup of the apatite group, or a group on its own. Following Strunz & Nickel (2001) we do prefer the latter option and we will speak throughout of the “britholite group”, which can be divided into two series: the britholite *sensu stricto* series ( $\Sigma REE > Ca$ ) and the calciobriholite series ( $Ca > \Sigma REE$ ).

The present paper is devoted to the description of fluorcalciobriholite, which was recently formally approved as a new mineral, together with its name, by the IMA Commission on New Minerals and Mineral Names (IMA No. 2006-010). Its detailed study, including a crystal structure determination, was completed on a non-metamict sample from Khibiny alkaline complex (Kola Peninsula, Russia), which is considered as the holotype specimen. Besides, some metamict samples from Sol'skoye REE deposit, Burpala and Ulan-Erge alkaline massif (three localities from Siberia, Russia), which we studied by means of electron microprobe and IR spectroscopy, were shown to correspond to fluorcalciobriholite. Among earlier published data on “britholite”, some samples from the alkaline massifs of Burpala (Buryatia, Siberia, Russia), Pichekhol' (Tuva, Siberia, Russia) (Vasil'eva, 1978), and Mushugai-Khuduk (Mongolia) (Ripp *et al.*, 2005), and from the volcanic ejecta of Vico complex (Latium, Italy) (Della Ventura *et al.*, 1999; Oberti *et al.*, 2001) correspond to fluorcalciobriholite.

The holotype specimen of fluorcalciobriholite from Khibiny has been deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow (registration no. 3420/1).

## Occurrence and general appearance

### Holotype sample

The holotype specimen of fluorcalciobriholite was collected in 1977 by one of us (YPM) in the eastern slope of Mount Kukisvumchorr, at the source of Tuliok river in Khibiny alkaline complex, Kola Peninsula, Russia. The mineral occurs

in thin (up to 1 cm) veinlets cross-cutting a fenitized gneiss xenolith situated in foyaites. The veinlets consist of coarse-grained aggregates of orthoclase, nepheline, sodalite, and biotite, which are up to 2–3 cm in length parallel to the elongation of the veinlets, and contain also smaller crystals of fayalite, gadolinite-(Ce), zircon, monazite-(Ce), zirconolite (“polymignite”), fluorcalciobriitholite, fluorapatite, fluorite, molybdenite, löllingite, and graphite. Fluorcalciobriitholite forms separate prismatic hexagonal crystals up to 10 mm in length and 0.5 mm across, embedded in colourless orthoclase, nepheline, and pink sodalite. The main crystal form is the hexagonal prism {10-10}. Crystals are badly terminated; only seldom the {0001} faces, imperfectly developed, were observed.

### Metamict samples

In Burpala alkaline massif (Northern Baikal Region, Buryatia, Siberia, Russia), fluorcalciobriitholite, together with visually indistinguishable fluorbriitholite-(Ce), occurs as massive fine-grained nodules up to 50 cm across in pegmatoid syenite. Fluorcalciobriitholite is associated with potassic feldspar, albite, alkali pyroxene, fluorapatite, and natrolite.

We also studied two samples stored in the collections of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow. A sample from Sol'skoye REE deposit, Buryatia, Siberia, Russia, with catalogue no. 62388 (donated in 1961 by A.I. Ginzburg) consists of a monomineral massive piece (10 cm in size) of fluorcalciobriitholite from alkaline metasomatic rock. Another sample from Ulan-Erge alkaline massif, Sangilen Uppland, Tuva, Siberia, Russia, with catalogue no. 67445 (donated in 1965 by V.I. Korokin) consists of a vial with grains (1–2 mm each) of fluorcalciobriitholite with calcite ingrowths, probably from alkaline metasomatite.

### Physical and optical properties

Crystalline fluorcalciobriitholite from Khibiny is transparent, with colour ranging from pale pinkish to brown, and with a white streak. The lustre is vitreous on the crystal faces and greasy on the broken surface. The mineral is brittle, with no observable cleavage, and conchoidal fracture. Mohs' hardness is 5.5. The density measured using volumetric method is 4.2(1) g/cm<sup>3</sup>, the calculated value using the empirical formula is 4.3 g/cm<sup>3</sup>. Metamict fluorcalciobriitholite from Siberian localities is translucent, the colour is brown (from reddish- to dark-brown), the streak is light brown, and the lustre is resinous. These metamict samples are strongly radioactive. Both crystalline and metamict varieties of fluorcalciobriitholite do not show fluorescence in ultraviolet light and cathodoluminescence.

Crystalline fluorcalciobriitholite from Khibiny is optically uniaxial (-), with  $\omega$  1.735(5),  $\epsilon$  1.730(5). Under a polarizing microscope, it is colourless, and non-pleochroic. Metamict samples from Siberia are optically isotropic or slightly anisotropic, with pale brown colour under microscope.

### Infrared spectroscopy

An infrared spectrum of the holotype fluorcalciobriitholite could not be obtained because of scarcity of material, and was recorded on the metamict sample from Ulan-Erge (Fig. 2). The sample was mixed with excess of anhydrous KBr, pelletized, and analysed using a Specord 75 IR spectrophotometer. IR spectrum of pure KBr-disk was subtracted from the overall spectrum. Polystyrene and gaseous NH<sub>3</sub> were used as frequency standards; the precision of frequency measurement is  $\pm 1$  cm<sup>-1</sup>; the mean resolution for the range 400–1600 cm<sup>-1</sup> is 1.2 cm<sup>-1</sup>. The IR spectrum of fluorcalciobriitholite is similar to the IR spectra of hydroxylbriitholite-(Ce) and hydroxylbriitholite-(Y). The main distinctive feature is the absence, in the spectrum of fluorcalciobriitholite, of any absorption band in the region of 3000–3800 cm<sup>-1</sup>, due to the absence of any (OH) groups substituting for F. Absorption bands (in cm<sup>-1</sup>; frequencies of the most intense bands are underlined; sh = shoulder, br = broad band) are: 1070sh, 1035sh, 930br, 600sh, 550sh, 500. The absorption contour in the range 800–1150 cm<sup>-1</sup> contains overlapping bands corresponding to Si-O (930 cm<sup>-1</sup>) and P-O (1070 and 1035 cm<sup>-1</sup>) stretching vibrations. The absorption curve in the range 400–650 cm<sup>-1</sup> contains bands corresponding to O-Si-O (500 cm<sup>-1</sup>) and O-P-O (600 and 550 cm<sup>-1</sup>) bending vibrations.

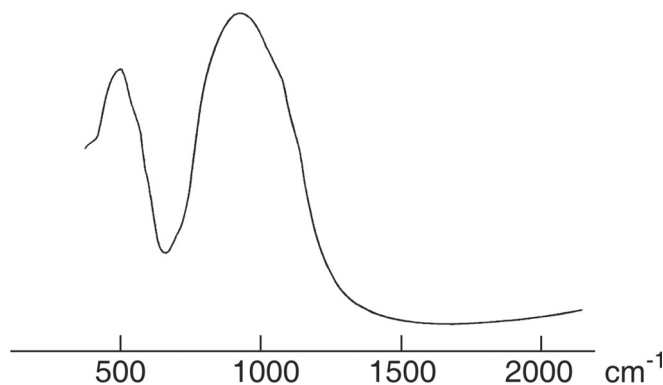


Fig. 2. IR spectrum of metamict fluorcalciobriitholite from Ulan-Erge.

### Chemical data

The chemical composition of fluorcalciobriitholite was studied by electron microprobe. Independent data obtained on the holotype specimen in three laboratories turned out to be well compatible between each other. The analytical data obtained using a Camebax SX 50 instrument in WDS mode (operating voltage 20 kV, estimated beam current 20 nA) are given in Table 1 (#1), together with data on metamict samples (#2–4). The electron beam was rastered over an area of 5x5  $\mu\text{m}^2$ . Standards used were: andradite (Ca, Fe, Si), SrSO<sub>4</sub> (Sr, S), MnTiO<sub>3</sub> (Mn), YPO<sub>4</sub> (Y), LaPO<sub>4</sub> (La), CePO<sub>4</sub> (Ce), PrPO<sub>4</sub> (Pr), NdPO<sub>4</sub> (Nd), SmPO<sub>4</sub> (Sm), GdPO<sub>4</sub> (Gd), DyPO<sub>4</sub> (Dy), ErPO<sub>4</sub> (Er), YbPO<sub>4</sub> (Yb), ThO<sub>2</sub> (Th), UO<sub>2</sub> (U), fluorapatite (P, F), vanadinite (Cl). H<sub>2</sub>O was not determined

Table 1. Chemical analyses (wt. %, above) and chemical compositions (a.p.f.u., below) of fluorcalciobrotholite.

	1	2	3	4	5	6	7	8	9
H <sub>2</sub> O					0.46	1.62			0.13
Na <sub>2</sub> O	bdl	bdl	bdl	bdl	0.06	0.22			bdl
K <sub>2</sub> O	bdl	nd	nd	nd	0.01	0.29			
CaO	21.89 (21.4-22.9)	17.02	18.64	16.69	18.14	18.20	20.78	15.27	16.80
MnO	0.34 (0.3-0.4)	bdl	bdl	bdl	0.10			0.11	0.18
SrO	0.25 (0.05-0.4)	nd	nd	nd	1.08	0.37			
B <sub>2</sub> O <sub>3</sub>									0.35
Al <sub>2</sub> O <sub>3</sub>	bdl	bdl	bdl	bdl	0.16	0.23			
Fe <sub>2</sub> O <sub>3</sub>	0.05 (0.00-0.1)	nd	nd	nd	0.05	0.41			
Y <sub>2</sub> O <sub>3</sub>	2.88 (2.6-3.2)	1.49	4.42	1.40	2.08	3.35	0.51	1.95	1.71
La <sub>2</sub> O <sub>3</sub>	12.36 (12.0-12.5)	12.82	8.13	13.98	14.90	11.43	18.67	10.30	11.23
Ce <sub>2</sub> O <sub>3</sub>	21.22 (20.9-21.5)	19.98	21.20	21.02	22.29	19.61	24.48	19.46	21.70
Pr <sub>2</sub> O <sub>3</sub>	1.86 (1.6-2.1)	1.93	2.46	1.88	2.63	2.27	2.11	1.78	2.19
Nd <sub>2</sub> O <sub>3</sub>	6.21 (5.8-6.6)	5.20	9.29	4.76	6.59	6.80	3.51	5.56	5.92
Sm <sub>2</sub> O <sub>3</sub>	0.82 (0.7-1.0)	1.24	2.36	0.99	0.30	1.65		0.90	0.72
Eu <sub>2</sub> O <sub>3</sub>									0.06
Gd <sub>2</sub> O <sub>3</sub>	0.74 (0.6-1.0)	nd	nd	nd	0.20	1.60		0.52	0.50
Dy <sub>2</sub> O <sub>3</sub>	0.61 (0.5-0.7)	nd	nd	nd	0.10	1.75		0.36	0.31
Ho <sub>2</sub> O <sub>3</sub>						0.67			
Er <sub>2</sub> O <sub>3</sub>	0.30 (0.0-0.4)	nd	nd	nd		1.75		0.17	0.14
Yb <sub>2</sub> O <sub>3</sub>	0.44 (0.2-0.6)	nd	nd	nd					0.12
ThO <sub>2</sub>	1.44 (1.1-1.8)	14.10	3.97	13.08	5.12	1.25		15.08	11.92
UO <sub>2</sub>	bdl	0.54	1.86	0.45	0.27	1.01		3.42	2.12
SiO <sub>2</sub>	16.24 (15.6-17.0)	18.47	19.51	18.96	18.14	19.35	17.90	20.27	21.10
TiO <sub>2</sub>								0.05	
P <sub>2</sub> O <sub>5</sub>	10.44 (10.1-10.7)	4.18	4.74	3.95	5.74	4.88	7.03		1.11
SO <sub>3</sub>	0.05 (0.00-0.1)	bdl	bdl	bdl			0.58		
F	2.02 (1.8-2.3)	1.66	1.81	1.70	1.91	2.51	1.75	1.68	2.12
Cl	0.06 (0.05-0.1)	nd	nd	nd					
-O=(F,Cl)	-0.86	-0.70	-0.76	-0.72	-0.80	-1.06	-0.74	-0.71	-0.89
<b>Total</b>	<b>99.36</b>	<b>97.93</b>	<b>97.63</b>	<b>98.14</b>	<b>99.28</b>	<b>100.16</b>	<b>96.58</b>	<b>96.17</b>	<b>99.54</b>
Na					0.02	0.05			
K					0.00	0.05			
<b>Ca</b>	<b>2.80</b>	<b>2.49</b>	<b>2.55</b>	<b>2.40</b>	<b>2.50</b>	<b>2.49</b>	<b>2.75</b>	<b>2.42</b>	<b>2.38</b>
Mn	0.03	–	–	–	0.01			0.01	0.02
Sr	0.02	–	–	–	0.08	0.03			
Al					0.02	0.03			
Fe	0.00	–	–	–	0.00	0.04			
Y	0.18	0.11	0.30	0.10	0.14	0.23	0.03	0.15	0.12
La	0.54	0.64	0.38	0.69	0.72	0.54	0.85	0.56	0.55
Ce	0.93	1.00	0.99	1.03	1.06	0.92	1.11	1.05	1.05
Pr	0.08	0.10	0.11	0.09	0.12	0.11	0.10	0.10	0.11
Nd	0.26	0.25	0.42	0.23	0.31	0.31	0.15	0.29	0.28
Sm	0.03	0.06	0.10	0.05	0.01	0.07		0.05	0.03
Eu									0.00
Gd	0.03	–	–	–	0.01	0.07		0.03	0.02
Dy	0.02	–	–	–	0.00	0.07		0.02	0.01
Ho						0.03			
Er	0.01	–	–	–		0.07		0.01	0.01
Yb	0.02	–	–	–					0.00
<b>Σ(Ln+Y)</b>	<b>2.12</b>	<b>2.16</b>	<b>2.31</b>	<b>2.20</b>	<b>2.38</b>	<b>2.41</b>	<b>2.24</b>	<b>2.26</b>	<b>2.19</b>

Table 1. (Cont.)

Ti								0.01	
Th	0.04	0.44	0.12	0.40	0.15	0.04		0.51	0.36
U	–	0.02	0.05	0.01	0.01	0.03		0.11	0.06
B									0.08
Si	1.94	2.52	2.49	2.55	2.37	2.47	2.21	3.00	2.79
P	1.06	0.48	0.51	0.45	0.63	0.53	0.74		0.12
S	0.00	–	–	–			0.05		
$\Sigma(\text{cations})$	<b>8.01</b>	<b>8.10</b>	<b>8.03</b>	<b>8.01</b>	<b>8.18</b>	<b>8.17</b>	<b>7.99</b>	<b>8.31</b>	<b>8.01</b>
F	0.76	0.72	0.73	0.72	0.79	1.01	0.68	0.79	0.89
Cl	0.01	–	–	–					
OH					0.21				0.11
O	12.25	12.51	12.25	12.39	12.36	12.18	12.20	12.67	12.05
$\Sigma(\text{anions})$	<b>13.03</b>	<b>13.23</b>	<b>12.98</b>	<b>13.11</b>	<b>13.36</b>	<b>13.19</b>	<b>12.88</b>	<b>13.46</b>	<b>13.05</b>
H <sub>2</sub> O					0.09	0.69			

Analyses 1–4: our electron microprobe data. 1. Khibiny (the holotype: averaged value of 7 point analyses; ranges are shown in parentheses); 2. Sol'skoye; 3. Ulan-Erge; 4. Burpala.

Analyses 5–9: data taken from literature (5–6: wet chemical data; 7–9: electron microprobe data). 5. Burpala (Vasil'eva *et al.*, 1978); 6. Pichekol' (Vasil'eva *et al.*, 1978); 7. Mushugai-Khuduk (Ripp *et al.*, 2005); 8. Vico (Della Ventura *et al.*, 1999); 9. Vico (Oberti *et al.*, 2001).

bdl = below detection limit, nd = not detected

All formulae were recalculated on the basis of 3 (Si+P+S+B). In analyses # 5, 6, and 9, OH was computed as (1-F). Excess hydrogen atoms, if any, were given as H<sub>2</sub>O.

Stoichiometric sums were rounded to the second digit after summing up the single stoichiometric terms; the latter are also presented in a rounded form, and this sometimes could give rise to apparent inconsistencies in the sums.

on the holotype specimen because of the scarcity of material. The absence of H<sub>2</sub>O in metamict fluorcalciobriitholite was confirmed by infrared spectroscopy (see above).

The empirical formula of the holotype specimen, based on [Si+P+S] = 3 *apfu*, is: [Ca<sub>2.80</sub>(Ce<sub>0.93</sub>La<sub>0.54</sub>Nd<sub>0.26</sub>Y<sub>0.18</sub>Pr<sub>0.08</sub>Sm<sub>0.03</sub>Gd<sub>0.03</sub>Dy<sub>0.02</sub>Yb<sub>0.02</sub>Er<sub>0.01</sub>) $\Sigma$ 2.12Th<sub>0.04</sub>Mn<sub>0.03</sub>Sr<sub>0.02</sub>] $\Sigma$ 5.01[(Si<sub>1.94</sub>P<sub>1.06</sub>) $\Sigma$ 3O<sub>12</sub>][F<sub>0.76</sub>O<sub>0.25</sub>Cl<sub>0.01</sub>] $\Sigma$ 1.02. The total number of anions very close to 13.00 in the empirical formula, calculated using the above mentioned basis (note that S is < 0.005 *apfu* and therefore is not present in the two-digit presentation of the formula), is a strong indication that there are no (OH) groups in the holotype specimen of fluorcalciobriitholite. The simplified formula is (Ca,REE)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>F. The ideal formula Ca<sub>3</sub>Ce<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)F (see Discussion) requires: CaO 24.08, Ce<sub>2</sub>O<sub>3</sub> 46.99, SiO<sub>2</sub> 17.20, P<sub>2</sub>O<sub>5</sub> 10.16, F 2.72, -O=F<sub>2</sub> 1.15, total 100.00 wt. %.

In Table 1 are also included (# 5–9) a few selected analyses taken from the literature, which correspond to fluorcalciobriitholite, since for all of them Ca prevails over  $\Sigma$ REE, and F is the dominating anion at the X site.

## X-ray crystallography and crystal structure

The X-ray powder-diffraction pattern of fluorcalciobriitholite is given in Table 2 and was obtained using a 114.6 mm diameter Debye-Scherrer camera, and Ni-filtered CuK $\alpha$ -radiation. The unit-cell dimensions refined from the powder data are: *a* = 9.554(3), *c* = 7.006(4) Å, *V* = 553.8(6) Å<sup>3</sup>, *Z* = 2.

A single crystal, selected under the microscope and preliminarily tested by Weissenberg photographs, was used for the intensity data collection which was carried out on a conventional four-circle Ital Structures diffractometer. The crystallographic features and the details of the X-ray dif-

fraction study and the structure refinement are given in Table 3. The unit cell parameters were determined by the least-squares method based on the angular parameters of 13 reflections in the range 9° < 2 $\theta$  < 22°. An empirical absorption correction was applied on the basis of  $\psi$ -scan measurements. The structure was refined against squared *F*'s in the space group *P6<sub>3</sub>/m* using the SHELX-97 program package (Sheldrick, 1997). The occupancy of Si vs. P was refined at the tetrahedrally coordinated site T, and the occupancy of Ca vs. Ce was refined at both independent larger sites M(1) and M(2). Trials to lower the symmetry to *P6<sub>3</sub>* did not result in any improvement of the structural model, and were eventually neglected.

The final positional and displacement parameters (anisotropic refinement for all atoms) are given in Table 4. The interatomic distances are listed in Table 5.

The basic features of the structure of fluorcalciobriitholite are common to all minerals of the apatite-briitholite family, and will not be discussed in detail here. It is worth noting that the average <T-O> distance (1.584 Å) is well consistent with the site population. The structural formula based on the refined site occupancies is the following: (Ca<sub>1.70</sub>REE<sub>1.30</sub>)(Ca<sub>1.31</sub>REE<sub>0.69</sub>)(Si<sub>0.65</sub>P<sub>0.35</sub>O<sub>4</sub>)<sub>3</sub>F. It is not perfectly balanced – although very close to balance: 25.04<sup>+</sup> vs. 25.00<sup>-</sup> charges – since we allowed a completely unconstrained refinement at all three cationic sites, and it is in fairly good agreement with the electron microprobe data.

## Discussion

Fluorcalciobriitholite is a member of the briitholite group, the analogue of fluorbriitholite-(Ce), (REE,Ca)<sub>5</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>F, with Ca prevailing over  $\Sigma$ REE. It can also be considered as

Table 2. X-ray powder-diffraction data for fluorcalciobriitholite.

$I_{\text{obs}}^*$	$d_{\text{obs}} (\text{\AA})$	$I_{\text{calc}}^{**}$	$d_{\text{calc}} (\text{\AA})$	$hkl$
10	4.10	28	4.137	200
45	3.51	32	3.503	002
70	3.15	40, 30	3.226, 3.127	102, 120
100	2.85	54, 100, 73	2.856, 2.856, 2.825	211, 121, 112
60	2.78	63	2.758	300
15	2.29	14	2.295	310
10	2.17	1, 2, 4	2.181, 2.181, 2.167	311, 131, 302
15	2.07	15, 6	2.098, 2.069	113, 400
25	1.965	43	1.973	222
20	1.931	18, 9	1.920, 1.920	312, 132
20	1.865	17, 35	1.871, 1.871	213, 123
15	1.785	38	1.781	402
10	1.738	22	1.752	004
10	1.654	1, 1	1.655, 1.644	500, 114
15	1.479	14	1.479	304
15	1.472	10, 2	1.473, 1.473	233, 323
10	1.443	8	1.450	332
25	1.236	12, 3	1.239, 1.239	522, 252
30	1.122	7, 3, 3	1.134, 1.127, 1.127	116, 235, 325
		2, 3, 8	1.120, 1.120, 1.120	702, 532, 352

\* – visual estimation

\*\* – calculated from the structural data

Table 3. Single crystal X-ray experimental data for fluorcalciobriitholite.

Diffractionmeter	Ital Structures
Radiation, wavelength ( $\text{\AA}$ )	MoK $\alpha$ , 0.71069
Working conditions	50 kV, 40 mA
Space group, Z	$P6_3/m, 2$
Unit-cell dimensions ( $\text{\AA}$ )	$a = 9.580(7), c = 6.985(4)$
Unit-cell volume ( $\text{\AA}^3$ )	555.2(7)
Crystal size ( $\text{mm}^3$ )	0.2 x 0.14 x 0.14
Index ranges	$-10 \leq h \leq 0, 0 \leq k \leq 12, 0 \leq l \leq 8$
$2\theta_{\text{max}}$ ( $^\circ$ )	54
Scan width ( $^\circ$ )	$\pm 0.5$
Scan speed ( $^\circ \text{min}^{-1}$ )	1 to 6
Measured reflections	2438
Independent reflections with $F_o > 4\sigma(F_o)$	343
$\mu$ ( $\text{mm}^{-1}$ )	9.89
$F(000)$	647.3
Refinement method	full-matrix least-squares on $F^2$
$R$ (on $F$ ), $wR$ (on $F^2$ ), GooF	0.0293; 0.0701; 1.121
Number of refined parameters	45
Largest residuals in the final $\Delta F$ map ( $e/\text{\AA}^3$ )	+0.65, -1.01

the analogue of fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , with Si prevailing over P (Table 6).

Two connected, heterovalent isomorphous substitution schemes are possible in the fluorapatite structure type:  $\text{Ca}^{2+} \leftrightarrow \text{REE}^{3+}$  and  $(\text{PO}_4)^{3-} \leftrightarrow (\text{SiO}_4)^{4-}$ ; they determine three possible fluorine-dominant mineral species in the system: 1. fluorapatite (Ca- and P-dominant), ideally  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ; 2. fluorbritholite-(REE) (REE- and Si-dominant), ideally  $\text{Ca}_2\text{REE}_3(\text{SiO}_4)_3\text{F}$ ; 3. fluorcalciobriitholite (Ca- and Si-dominant), ideally  $\text{Ca}_3\text{REE}_2(\text{SiO}_4)_2(\text{PO}_4)\text{F}$ . The fourth species, REE- and P-dominant, can not exist due to charge constraints. For the ideal formulae, the limits in this system must be the following: 1) a limit between fluorbritholite-

(REE) and fluorcalciobriitholite ( $\text{Ca} = \Sigma\text{REE}$ ):  $\text{Ca}_{2.5}\text{REE}_{2.5}(\text{SiO}_4)_{2.5}(\text{PO}_4)_{0.5}\text{F}$ ; 2) a limit between fluorcalciobriitholite and fluorapatite ( $\text{Si} = \text{P}$ ):  $\text{Ca}_{3.5}\text{REE}_{1.5}(\text{SiO}_4)_{1.5}(\text{PO}_4)_{1.5}\text{F}$ .

In case of presence of significant amounts of tetravalent cations (Th, U) substituting for Ca and REE, the Si:P ratio in the mineral can increase. Analysis of a sample from Vico (Latium, Italy; #8 in Table 1), corresponding to the ideal formula  $\text{Ca}_{2.5}\text{REE}_2\text{Th}_{0.5}(\text{SiO}_4)_3\text{F}$ , shows the possible existence of a P-free variety of fluorcalciobriitholite, if the content of tetravalent cations is high. In general, we can argue a solid solution series between fluorcalciobriitholite and the hypothetical phase  $\text{Ca}_{3.5}(\text{Th,U})_{1.5}(\text{SiO}_4)_3\text{F}$ . The latter can be con-

Table 4. Final fractional coordinates, site occupancies and displacement parameters for fluorcalciobriitholite.

Site	Site occupancy factors	x	y	z	$U_{eq}$
T	Si <sub>0.325(2)</sub> P <sub>0.175(2)</sub>	0.3718(3)	0.4001(3)	0.25	0.0261(6)
M(1)	Ca <sub>0.218(2)</sub> Ce <sub>0.115(2)</sub>	0.33333	0.66667	0.0006(2)	0.0311(4)
M(2)	Ca <sub>0.283(4)</sub> Ce <sub>0.217(4)</sub>	0.2487(1)	0.0107(1)	0.25	0.0330(3)
O(1)	O <sub>0.5</sub>	0.4677(8)	0.5906(8)	0.25	0.043(2)
O(2)	O <sub>0.5</sub>	0.4866(8)	0.3255(9)	0.25	0.037(2)
O(3)	O <sub>1.0</sub>	0.2563(6)	0.3432(8)	0.4310(7)	0.054(2)
F	F <sub>0.16667</sub>	0	0	0.25	0.092(5)

Site	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
T	0.028(1)	0.031(1)	0.022(1)	0	0	0.017(1)
M(1)	0.0367(5)	0.0367(5)	0.0200(6)	0	0	0.0183(2)
M(2)	0.0366(5)	0.0310(5)	0.0258(5)	0	0	0.0126(4)
O(1)	0.037(3)	0.032(3)	0.056(5)	0	0	0.014(3)
O(2)	0.036(3)	0.057(4)	0.030(3)	0	0	0.032(3)
O(3)	0.048(3)	0.098(5)	0.034(3)	0.028(3)	0.013(2)	0.049(3)
F	0.058(5)	0.058(5)	0.159(15)	0	0	0.029(2)

Table 5. Selected interatomic distances (Å) in the structure of fluorcalciobriitholite.

T – O(1)	1.581(7)	M(1) – O(2)	2.432(4) x 3	M(2) – F	2.333(2)
T – O(2)	1.583(6)	M(1) – O(1)	2.482(5) x 3	M(2) – O(3)	2.378(5) x 2
T – O(3)	1.587(5) x 2	M(1) – O(3)	2.844(7) x 3	M(2) – O(1)	2.445(7)
				M(2) – O(3)'	2.565(5) x 2
				M(2) – O(2)	2.723(8)
Average	1.584	Average	2.586	Average	2.484

Table 6. Comparative data on fluorine-dominant calcium and rare-earth silicate, sulfate and phosphate minerals with apatite-type structure.

Mineral Formula	Fluorcalciobriitholite (Ca,REE) <sub>5</sub> [(Si,P)O <sub>4</sub> ] <sub>3</sub> F	Fluorbritholite-(Ce) (REE,Ca) <sub>5</sub> [(Si,P)O <sub>4</sub> ] <sub>3</sub> F	Fluorellestadite Ca <sub>10</sub> (SO <sub>4</sub> ) <sub>3</sub> (SiO <sub>4</sub> ) <sub>3</sub> F <sub>2</sub> *	Fluorapatite Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F
Crystal system	Hexagonal	Hexagonal	Hexagonal (?)	Hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$ (**)	$P6_3/m$
a, Å	9.580	9.517	9.485	9.397
c, Å	6.985	6.983	6.916	6.878
Z	2	2	1	2
$\omega$	1.735	1.792	1.638	1.631 – 1.650
$\epsilon$	1.730	1.786	1.632	1.627 – 1.646
Optical sign	(-)	(-)	(-)	(-)
Reference	this work	Gu <i>et al.</i> , 1994	Chesnokov <i>et al.</i> , 1987	Anthony <i>et al.</i> , 2000

\* – the empirical formula of the holotype specimen of fluorellestadite from Kopeisk, South Urals, Russia, is:

(Ca<sub>9.97</sub>Mn<sub>0.03</sub>)<sub>Σ10.00</sub>[(SO<sub>4</sub>)<sub>2.84</sub>(SiO<sub>4</sub>)<sub>2.79</sub>(PO<sub>4</sub>)<sub>0.20</sub>(CO<sub>3</sub>)<sub>0.17</sub>]<sub>Σ6.00</sub>F<sub>2.08</sub>O<sub>0.07</sub> (Chesnokov *et al.*, 1987), *i.e.*, it is formally a sulfate-dominant mineral.

\*\* – the crystal structure was not studied, the space group symmetry was supposed by analogy with fluorapatite (Chesnokov *et al.*, 1987); however the symmetry of hydroxyllellestadite, Ca<sub>10</sub>(SO<sub>4</sub>)<sub>3</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>, is pseudo-hexagonal monoclinic:  $P2_1/m$  (Sudarsanan, 1980; Hughes & Drexler, 1991) or  $P2_1$  (Organova *et al.*, 1994).

sidered as fluorine-dominant analogue of the phase Ca<sub>3.5</sub>(Th,U)<sub>1.5</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH) reported by Jamtveit *et al.* (1997) in alkaline-calcareous metamorphic rocks from the Oslo Rift, Southern Norway, which forms a solid solution series with hydroxylbriitholite-(Ce).

It is also not excluded that the X position in briitholites – calciobriitholites can be partially occupied by O<sup>2-</sup> and/or vacant. This assumption is based on the existence of some synthetic apatite-type compounds in the system Ca–REE–Si–P,

namely Ca<sub>6</sub>La<sub>4</sub>(SiO<sub>4</sub>)<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O<sup>□</sup>, Ca<sub>4</sub>La<sub>6</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sup>□</sup> (Boyer *et al.*, 1997), Ca<sub>6</sub>La<sub>2</sub>Ce<sub>2</sub>(SiO<sub>4</sub>)<sub>6</sub> (Cockbain & Smith, 1967), Ca<sub>6</sub>La<sub>4</sub>(SiO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>O<sub>2</sub>, Ca<sub>2</sub>La<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> (Ito, 1968), and some others (*e.g.*, with other REE). The latter compound can be considered as the synthetic analogue of a hypothetical “oxybriitholite” end-member, and the compound Ca<sub>6</sub>REE<sub>4</sub>(SiO<sub>4</sub>)<sub>6</sub> is the synthetic analogue of a hypothetical X-vacant calciobriitholite end-member. The compound Ca<sub>6</sub>REE<sub>4</sub>(SiO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>O<sub>2</sub> can be considered as a REE,Si-

bearing “oxyapatite”. Note that a significant incorporation of the “oxybritholite” component could take place in britholite-(Ce) from Monte Somma, Vesuvius, Italy, formed under high temperature and relatively low pressure (Orlandi *et al.*, 1989). The holotype specimen of fluorcalciobrihtholite contains 0.25 O *apfu*.

Thus, in the “simplified” system (*i.e.*, without the substitutions involving tetravalent cations Th and U, and O<sup>2-</sup> and vacancy in the X position), the fluorapatite composition field falls within the limits of Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F – Ca<sub>3.5</sub>REE<sub>1.5</sub>(SiO<sub>4</sub>)<sub>1.5</sub>(PO<sub>4</sub>)<sub>1.5</sub>F, and the fluorbritholite-(REE) field falls within the limits of REE<sub>3</sub>Ca<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>F – Ca<sub>2.5</sub>REE<sub>2.5</sub>(SiO<sub>4</sub>)<sub>2.5</sub>(PO<sub>4</sub>)<sub>0.5</sub>F. The fluorcalciobrihtholite field lies within the limits Ca<sub>2.5</sub>REE<sub>2.5</sub>(SiO<sub>4</sub>)<sub>2.5</sub>(PO<sub>4</sub>)<sub>0.5</sub>F – Ca<sub>3.5</sub>REE<sub>1.5</sub>(SiO<sub>4</sub>)<sub>1.5</sub>(PO<sub>4</sub>)<sub>1.5</sub>F; the formula of idealized (“mid-member”) fluorcalciobrihtholite is considered as Ca<sub>3</sub>REE<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)F. Its La-dominant analogue, Ca<sub>3</sub>La<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)F, (space group P6<sub>3</sub>/m) is known as a synthetic compound (Boyer *et al.*, 1997).

In the above ideal substitution scheme, no more than 3 REE per formula unit can be accommodated within the britholite structure, due to charge constraints. As it can be seen in Fig. 1b, there exist analyses of britholites with REE > 3. In those cases the charge balance can be achieved, as discussed above, by incorporation of substantial O<sup>2-</sup> at the X position, in place of monovalent anions (F<sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>). Theoretically, also the substitution mechanism Ca<sup>2+</sup> ↔ (Na,K)<sup>+</sup> could play some role in obtaining balanced formulae, but its extent in natural britholites seems definitely minor.

The simplified structural formula of fluorcalciobrihtholite is (Ca,REE)<sub>2</sub>(Ca,REE)<sub>3</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>F, whereas in hydroxylbritholite-(Ce) and hydroxylbritholite-(Y) REE prevail over Ca at both independent larger cation sites: (REE,Ca)<sub>2</sub>(REE,Ca)<sub>3</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>(OH,F), (Genkina *et al.*, 1991; Noe *et al.*, 1993) or at either: (Ca,REE)<sub>2</sub>(REE,Ca)<sub>3</sub>[(Si,P)O<sub>4</sub>]<sub>3</sub>(OH,F) (Noe *et al.*, 1993).

The relationship of apatite with other related Si-bearing Ca-dominant mineral species, namely ellestadites, Ca<sub>5</sub>(SO<sub>4</sub>)<sub>1.5</sub>(SiO<sub>4</sub>)<sub>1.5</sub>X, (X = OH<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>), is characterized by another isomorphous substitution scheme: 2(PO<sub>4</sub>)<sup>3-</sup> ↔ (SiO<sub>4</sub>)<sup>4-</sup> + (SO<sub>4</sub>)<sup>2-</sup>. Minerals of the britholite and the ellestadite series plot in quite different fields within the compositional diagrams P – Si – S and Ca – ΣREE (Fig. 1). Due to charge-balance constraints, minerals of the ellestadite series are practically REE-free, and have a (SO<sub>4</sub>)/(SiO<sub>4</sub>) ratio close to 1. Note that almost all of the known analyses of natural ellestadites, including the only published quantitative analysis of fluorellestadite, Ca<sub>5</sub>(SO<sub>4</sub>)<sub>1.5</sub>(SiO<sub>4</sub>)<sub>1.5</sub>F, have S prevailing over Si, *i.e.*, ellestadites (assuming a disordered distribution of S and Si in the tetrahedral sites) can be formally considered as sulfates rather than silicates.

A final remark seems appropriate: it is not excluded that some analyses of “britholite” reported in literature, with Ca > ΣREE and in which F was not detected, actually correspond to fluorcalciobrihtholite. This could be the case, among others, for samples from Madagascar (Kieft & Burke, 1970), Monte Somma, Italy (Orlandi *et al.*, 1989), and Khibiny, Kola Peninsula, Russia (Yakovenchuk *et al.*, 2005).

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## References

- Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C. (2000): Handbook of mineralogy. Vol. IV: Arsenates, phosphates, vanadates. Mineral Data Publishing, Tucson, 680 p.
- Bayliss, P. & Levinson, A.A. (1988): A system of nomenclature for rare earth mineral species: revision and extension. *Am. Mineral.*, **73**, 422–423.
- Boyer, L., Carpena, J., Lacout, J.L. (1997): Synthesis of phosphate-silicate apatites at atmospheric pressure. *Solid State Ionics*, **95**, 121–129.
- Chesnokov, B.V., Bazhenova, L.F., Bushmakin, A.F. (1987): Fluorellestadite, Ca<sub>10</sub>[(SO<sub>4</sub>),(SiO<sub>4</sub>)]<sub>6</sub>F<sub>2</sub> – a new mineral. *Zap. Vser. Mineral. Obsh.*, **116**, 743–746 (in Russian).
- Cockbain, A.G. & Smith, G.V. (1967): Alkaline-earth-rare-earth silicate and germanate apatites. *Mineral. Mag.*, **36**, 411–421.
- Della Ventura, G., Williams, C.T., Cabella, R., Oberti, R., Caprilli, E., Bellatreccia, F. (1999): Britholite-hellandite intergrowths and associated REE minerals from the alkali-syenitic ejecta of the Vico volcanic complex (Latium, Italy): petrological implications bearing on REE mobility in volcanic systems. *Eur. J. Mineral.*, **11**, 843–855.
- Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. (1997): Dana’s new mineralogy. Wiley, New York, 1819 p.
- Gay, P. (1957): An X-ray investigation of some rare-earth silicates: cerite, lessingite, beckelite, britholite and stillwellite. *Mineral. Mag.*, **31**, 455–468.
- Genkina, E.A., Malinovskii, Yu.A., Khomyakov, A.P. (1991): Crystal structure of Sr-containing britholith. *Sov. Phys. Crystallogr.*, **36**, 19–21.
- Gu, J., Chao, G.Y., Tang, S. (1994): A new mineral – fluorbritholite-(Ce). *J. Wuhan Univ. Technol.*, **9**, 1855–1866.
- Hata, S. (1938): Abukumalite, a new mineral from pegmatites of Isaka, Fukushima prefecture. *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **34**, 1018–1023.
- Hughes, J.M. & Drexler, J.W. (1991): Cation substitution in the apatite tetrahedral site: crystal structures of type ellestadite and type ferromite. *N. Jb. Mineral. Mh.*, **1991**, 327–336.
- Ito, J. (1968): Silicate apatites and oxyapatites. *Am. Mineral.*, **53**, 890–907.
- Jamtveit, B., Dahlgren, S., Austrheim, H. (1997): High-grade contact metamorphism of calcareous rocks from the Oslo Rift, Southern Norway. *Am. Mineral.*, **82**, 1241–1254.
- Kalsbeek, N., Larsen, S., Rønso, J.G. (1990): Crystal structures of rare earth elements rich apatite analogues. *Z. Kristallogr.*, **191**, 249–263.

- Kapustin, Yu.L. (1986): On accessory minerals of the briholite group in alkaline rocks of Tuva. *New Data on Minerals*, **33**, 53–63 (in Russian).
- Kieft, C. & Burke, E.A.J. (1970): La briholite, un minéral nouveau pour Madagascar. *Compt. Rend. Semaine Géol. Madagascar*, 101–103.
- Kupriyanova, I.I., Sidorenko, G.A., Kudrina, M.A. (1966): Briholite group minerals. *Geology of Deposits of Rare Elements*, **26**, 23–66 (in Russian).
- Lazarenko, E.K., Lavrinenko, L.F., Buchinskaya, N.I., Galiy, S.A., Voznyak, D.K., Galaburda, Y.A., Zatsikha, B.V., Ivanova, A.V., Kvasnitsa, V.N., Kul'chitskaya, A.A., Kuts, V.P., Mel'nikov, V.S., Pavlishin, V.I., Turkevich, G.I. (1981): The mineralogy of Azov Sea region. Naukova Dumka Publishing, Kiev, 432 p. (in Russian).
- Levinson, A.A. (1966): A system of nomenclature for rare-earth minerals. *Am. Mineral.*, **51**, 152–158.
- Li, D., Wang, P., Li, J. (1981): The crystal-structure of lessingite, rich in light rare earth of cerium. *Acta Crystallogr.*, **A37**, suppl., C188.
- Nekrasova, R.A. & Nekrasov, I.Ya. (1980): A new data on briholite group minerals. in "Geochemistry. Mineralogy. 26th International Geological Congress: Reports of Soviet Geologists", F.V. Chukhrov & V.L. Barsukov, eds. Nauka Publishing, Moscow, 170–176 (in Russian).
- Noe, D.C., Hughes, J.M., Mariano, A.M., Drexler, J.W., Kato, A. (1993): The crystal structure of monoclinic briholite-(Ce) and briholite-(Y). *Z. Kristallogr.*, **206**, 233–246.
- Oberti, R., Ottolini, L., Della Ventura, G., Parodi, G.C. (2001): On the symmetry and crystal chemistry of briholite: new structural and microanalytical data. *Am. Mineral.*, **86**, 1066–1075.
- Organova, N.I., Rastsvetaeva, R.K., Kuz'mina, O.V., Arapova, G.A., Litsarev, M.A., Fin'ko, V.I. (1994): Crystal structure of low-symmetry ellestadite in comparison with other apatite-like structures. *Kristallogr.*, **39**, 278–282 (in Russian).
- Orlandi, P., Perchiazzi, N., Mannucci, G. (1989): First occurrence of briholite-(Ce) in Italy (Monte Somma, Vesuvius). *Eur. J. Mineral.*, **1**, 723–725.
- Ripp, G.S., Karmanov, N.S., Kanakin, S.V., Doroshkevich, A.G., Andreev, G.V. (2005): Cerium briholite from Mushugai ore deposit (Mongolia). *Zap. Vser. Mineral. Obsh.*, **134**, 90–103 (in Russian).
- Rouse, R.C. & Dunn, P.J. (1982): A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites. *Am. Mineral.*, **67**, 90–96.
- Sheldrick, G.M. (1997): SHELXL-97 and SHELXS-97: Programs for crystal structure determination. Univ. of Göttingen, Germany.
- Solodov, N.A., Usova, T.Yu., Osokin, E.D., Pavlova, V.N., Semenov, E.I., Skosyreva, M.V., Solodova, Yu.P., Torikova, M.V., Tsyganov, A.E. (1991): Non-traditional type of rare-metal mineral resources. Nedra Publishing, Moscow, 248 p. (in Russian).
- Strunz, H. & Nickel, E.H. (2001): Strunz mineralogical tables: Chemical-structural mineral classification system, 9<sup>th</sup> ed. Schweizerbart'sche, Stuttgart, 870 p.
- Sudarsanan, K. (1980): Structure of hydroxyllelestadite. *Acta Crystallogr.*, **B36**, 1636–1639.
- Vasil'eva, Z.V. (1978): Chemical composition and typomorphic features of briholite. in: "Composition and structure of minerals as indicators of their genesis", F.V. Chukhrov & N.V. Petrovskaya, eds. Nauka Publishing, Moscow, 109–124 (in Russian).
- Winther, C. (1901): Briholith, a new mineral. *Medd. Grønl.*, **24**, 190–196.
- Yakovenchuk, V., Ivanyuk, G., Pakhomovsky, Ya., Men'shikov, Yu. (2005): Khibiny. Laplandia Minerals Ltd., Apatity, 468 p.
- Zhang, J., Fang, Z., Liao, L. (1992): A study of crystal structure of briholite-Y. *Acta Mineral. Sinica*, **12**, 131–142.

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