Fluorcalciobritholite, (Ca,REE)₅[(Si,P)O₄]₃F, a new mineral: description and crystal chemistry

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Abstract: The new mineral fluorcalciobritholite, ideally $Ca_3Ce_2(SiO_4)_2(PO_4)F$, 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. Fluorcalciobritholite 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/cm³. 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*: $[Ca_{2.80} (Ce_{0.93}La_{0.54}Nd_{0.26}Y_{0.18}Pr_{0.08}Sm_{0.03}Gd_{0.03}Dy_{0.02}Yb_{0.02}Er_{0.01})_{\Sigma2.12} Th_{0.04}Mn_{0.03} Sr_{0.02}]_{\Sigma4.99} [(Si_{1.94}P_{1.06})_{\Sigma3}O_{12}] [F_{0.76}O_{0.22}Cl_{0.01}]_{\Sigma0.99}$ (Z = 2). The IR spectrum of metamict fluorcalciobritholite from Siberia showed a marked similarity with those of hydroxylbritholite-(Ce) and hydroxylbritholite-(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 $P6_3/m$, with a = 9.580(7), c = 6.985(4) Å, V = 555.2(7) Å³. The crystal structure was refined from single-crystal X-ray diffraction data to R_F = 0.029. Fluorcalciobritholite, whose simplified formula is (Ca,REE)₅[(Si,P)O₄]₃F, differs from fluorbritholite in having Ca > ΣREE, and differs from fluorapatite in having Si > P. Its compositional field falls within the limits $Ca_{2.5}REE_{2.5}(SiO_4)_{2.5}(PO_4)_{0.5}F$ (boundary with fluorbritholite) and $Ca_{3.5}REE_{1.5}(SiO_4)_{1.5}(PO_4)_{1.5}F$ (boundary with fluorapatite). Both the mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names.

Key-words: fluorcalciobritholite, new mineral, crystal structure, Khibiny alkaline complex, britholite group, apatite group.

Introduction

Britholites are silicates (typically phosphorus-bearing) with apatite-type structure and the general formula (REE,Ca)₅[(Si,P)O₄]₃*X*, where REE include yttrium, as usual, and *X* = (OH)⁻, F⁻, or Cl⁻. So far hydroxylbritholite-(Ce), (Ce,Ca)₅[(Si,P)O₄]₃(OH) (synonyms: beckelite, lessingite, pravdite), hydroxylbritholite-(Y)*, (Y,Ca)₅[(Si,P)O₄]₃(OH)

(formerly abukumalite), and fluorbritholite-(Ce), (Ce,Ca)₅[(Si,P)O₄]₃F are considered as valid mineral species (Winther, 1901; Hata, 1938; Levinson, 1966; Gu *et al.*, 1994). Britholites are hexagonal with space group $P6_3/m$ or $P6_3$, or monoclinic pseudo-hexagonal with space group $P2_1$ (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.

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

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* We are aware that in the mineralogical literature (see, for instance, Gaines *et al.*, 1997) these minerals are referred to as britholite-(Ce) and britholite-(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 britholites, as it was already done for apatites.
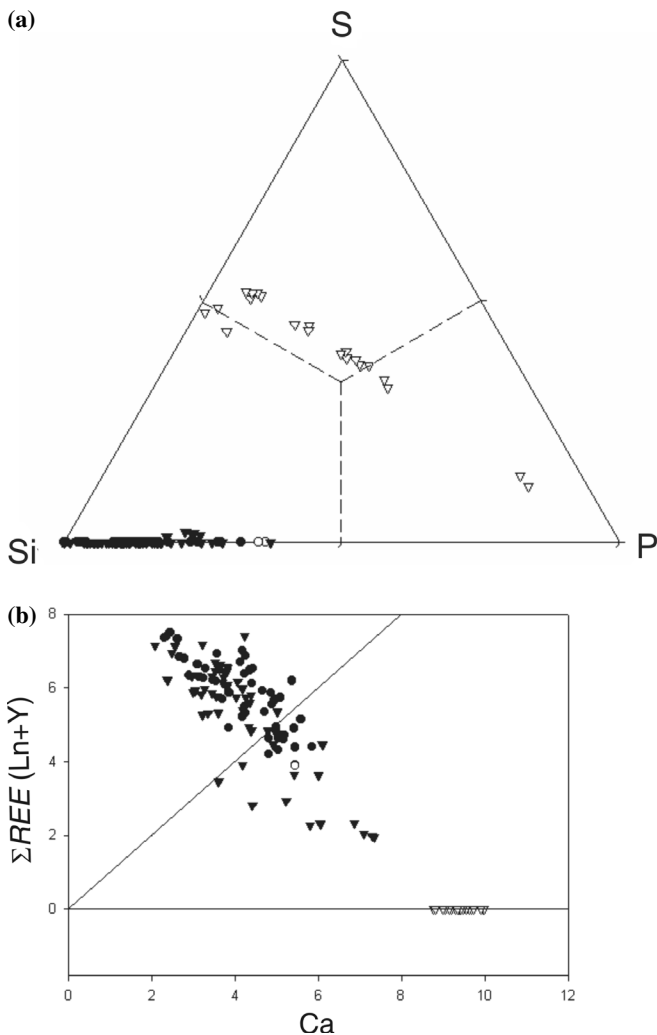
(a)

(b)

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 fluorcalciobritholite 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 "bri-

tholite" 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 ΣREE. 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 calciobritholite 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 (ΣREE > Ca) and the calciobritholite series (Ca > ΣREE).

The present paper is devoted to the description of fluorcalciobritholite, 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 fluorcalciobritholite. 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 fluorcalciobritholite.

The holotype specimen of fluorcalciobritholite 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 fluorcalciobritholite 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"), fluorcalciobritholite, fluorapatite, fluorite, molybdenite, löllingite, and graphite. Fluorcalciobritholite 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), fluorcalciobritholite, together with visually indistinguishable fluorbritholite-(Ce), occurs as massive fine-grained nodules up to 50 cm across in pegmatoid syenite. Fluorcalciobritholite 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 fluorcalciobritholite 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. Korkin) consists of a vial with grains ($1-2$ mm each) of fluorcalciobritholite with calcite ingrowths, probably from alkaline metasomatite.

Physical and optical properties

Crystalline fluorcalciobritholite 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^3, the calculated value using the empirical formula is 4.3 g/cm^3. Metamict fluorcalciobritholite 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 fluorcalciobritholite do not show fluorescence in ultraviolet light and cathodoluminescence.

Crystalline fluorcalciobritholite from Khibiny is optically uniaxial (-), with ω 1.735(5), ε 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 fluorcalciobritholite 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_3 were used as frequency standards; the precision of frequency measurement is ± 1 cm^{-1}; the mean resolution for the range $400-1600$ cm^{-1} is 1.2 cm^{-1}. The IR spectrum of fluorcalciobritholite is similar to the IR spectra of hydroxylbritholite-(Ce) and hydroxylbritholite-(Y). The main distinctive feature is the absence, in the spectrum of fluorcalciobritholite, of any absorption band in the region of $3000-3800$ cm^{-1}, due to the absence of any (OH) groups substituting for F. Absorption bands (in cm^{-1}; 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^{-1} contains overlapping bands corresponding to Si-O (930 cm^{-1}) and P-O (1070 and 1035 cm^{-1}) stretching vibrations. The absorption curve in the range $400-650$ cm^{-1} contains bands corresponding to O-Si-O (500 cm^{-1}) and O-P-O (600 and 550 cm^{-1}) bending vibrations.
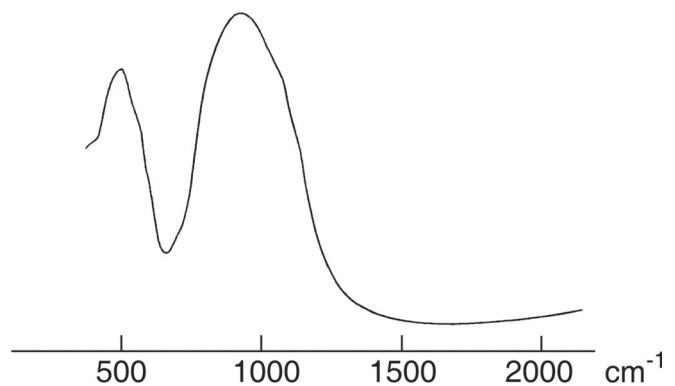
Fig. 2. IR spectrum of metamict fluorcalciobritholite from Ulan-Erge.

Chemical data

The chemical composition of fluorcalciobritholite 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 μm^2. Standards used were: andradite (Ca, Fe, Si), $SrSO_4$ (Sr, S), $MnTiO_3$ (Mn), YPO_4 (Y), $LaPO_4$ (La), $CePO_4$ (Ce), $PrPO_4$ (Pr), $NdPO_4$ (Nd), $SmPO_4$ (Sm), $GdPO_4$ (Gd), $DyPO_4$ (Dy), $ErPO_4$ (Er), $YbPO_4$ (Yb), ThO_2 (Th), UO_2 (U), fluorapatite (P, F), vanadinite (Cl). H_2O was not determined

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

	1	2	3	4	5	6	7	8	9
H_2O					0.46	1.62			0.13
Na_2O	bdl	bdl	bdl	bdl	0.06	0.22			bdl
K_2O	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_2O_3									0.35
Al_2O_3	bdl	bdl	bdl	bdl	0.16	0.23			
Fe_2O_3	0.05 (0.00-0.1)	nd	nd	nd	0.05	0.41			
Y_2O_3	2.88 (2.6-3.2)	1.49	4.42	1.40	2.08	3.35	0.51	1.95	1.71
La_2O_3	12.36 (12.0-12.5)	12.82	8.13	13.98	14.90	11.43	18.67	10.30	11.23
Ce_2O_3	21.22 (20.9-21.5)	19.98	21.20	21.02	22.29	19.61	24.48	19.46	21.70
Pr_2O_3	1.86 (1.6-2.1)	1.93	2.46	1.88	2.63	2.27	2.11	1.78	2.19
Nd_2O_3	6.21 (5.8-6.6)	5.20	9.29	4.76	6.59	6.80	3.51	5.56	5.92
Sm_2O_3	0.82 (0.7-1.0)	1.24	2.36	0.99	0.30	1.65		0.90	0.72
Eu_2O_3									0.06
Gd_2O_3	0.74 (0.6-1.0)	nd	nd	nd	0.20	1.60		0.52	0.50
Dy_2O_3	0.61 (0.5-0.7)	nd	nd	nd	0.10	1.75		0.36	0.31
Ho_2O_3						0.67			
Er_2O_3	0.30 (0.0-0.4)	nd	nd	nd		1.75		0.17	0.14
Yb_2O_3	0.44 (0.2-0.6)	nd	nd	nd					0.12
ThO_2	1.44 (1.1-1.8)	14.10	3.97	13.08	5.12	1.25		15.08	11.92
UO_2	bdl	0.54	1.86	0.45	0.27	1.01		3.42	2.12
SiO_2	16.24 (15.6-17.0)	18.47	19.51	18.96	18.14	19.35	17.90	20.27	21.10
TiO_2								0.05	
P_2O_5	10.44 (10.1-10.7)	4.18	4.74	3.95	5.74	4.88	7.03		1.11
SO_3	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
Total	**99.36**	**97.93**	**97.63**	**98.14**	**99.28**	**100.16**	**96.58**	**96.17**	**99.54**
Na					0.02	0.05			
K					0.00	0.05			
Ca	**2.80**	**2.49**	**2.55**	**2.40**	**2.50**	**2.49**	**2.75**	**2.42**	**2.38**
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	023	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
Σ(*Ln*+Y)	**2.12**	**2.16**	**2.31**	**2.20**	**2.38**	**2.41**	**2.24**	**2.26**	**2.19**

Table 1. (Cont.)

	1	2	3	4	5	6	7	8	9
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		
Σ(cations)	**8.01**	**8.10**	**8.03**	**8.01**	**8.18**	**8.17**	**7.99**	**8.31**	**8.01**
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
Σ(anions)	**13.03**	**13.23**	**12.98**	**13.11**	**13.36**	**13.19**	**12.88**	**13.46**	**13.05**
H₂O					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. Pichekhol' (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 H₂O.

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_2O in metamict fluorcalciobritholite was confirmed by infrared spectroscopy (see above).

The empirical formula of the holotype specimen, based on [Si+P+S] = 3 *apfu*, is: $[Ca_{2.80}(Ce_{0.93}La_{0.54}Nd_{0.26}Y_{0.18}Pr_{0.08}Sm_{0.03}Gd_{0.03}Dy_{0.02}Yb_{0.02}Er_{0.01})_{\Sigma2.12}Th_{0.04}Mn_{0.03}Sr_{0.02}]_{\Sigma5.01}[(Si_{1.94}P_{1.06})_{\Sigma3}O_{12}][F_{0.76}O_{0.25}Cl_{0.01}]_{\Sigma1.02}$. 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 fluorcalciobritholite. The simplified formula is $(Ca,REE)_5[(Si,P)O_4]_3F$. The ideal formula $Ca_3Ce_2(SiO_4)_2(PO_4)F$ (see Discussion) requires: CaO 24.08, Ce_2O_3 46.99, SiO_2 17.20, P_2O_5 10.16, F 2.72, -O=F_2 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 fluorcalciobritholite, since for all of them Ca prevails over ΣREE, and F is the dominating anion at the *X* site.

X-ray crystallography and crystal structure

The X-ray powder-diffraction pattern of fluorcalciobritholite is given in Table 2 and was obtained using a 114.6 mm diameter Debye-Scherrer camera, and Ni-filtered Cu*K*α-radiation. The unit-cell dimensions refined from the powder data are: *a* = 9.554(3), *c* = 7.006(4) Å, *V* = 553.8(6) Å³, *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 diffraction 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° < 2θ < 22°. An empirical absorption correction was applied on the basis of ψ-scan measurements. The structure was refined against squared *F*'s in the space group *P*6₃/*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 *P*6₃ 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 fluorcalciobritholite are common to all minerals of the apatite-britholite 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: $(Ca_{1.70}REE_{1.30})(Ca_{1.31}REE_{0.69})(Si_{0.65}P_{0.35}O_4)_3F$. It is not perfectly balanced – although very close to balance: 25.04⁺ *vs.* 25.00⁻ 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

Fluorcalciobritholite is a member of the britholite group, the analogue of fluorbritholite-(Ce), $(REE,Ca)_5[(Si,P)O_4]_3F$, with Ca prevailing over ΣREE. It can also be considered as

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

I_{obs}*	d_{obs} (Å)	I_{calc}**	d_{calc} (Å)	$h\,k\,l$
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 fluorcalciobritholite.

Diffractometer	Ital Structures
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71069
Working conditions	50 kV, 40 mA
Space group, Z	$P6_3/m$, 2
Unit-cell dimensions (Å)	a = 9.580(7), c = 6.985(4)
Unit-cell volume (Å^3)	555.2(7)
Crystal size (mm^3)	0.2 x 0.14 x 0.14
Index ranges	$-10 \le h \le 0, 0 \le k \le 12, 0 \le l \le 8$
$2\theta_{max}$ (°)	54
Scan width (°)	±0.5
Scan speed (° min^{-1})	1 to 6
Measured reflections	2438
Independent reflections with $F_o > 4\sigma(F_o)$	343
μ (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 ΔF map (e/Å^3)	+0.65, -1.01

the analogue of fluorapatite, $Ca_5(PO_4)_3F$, with Si prevailing over P (Table 6).

Two connected, heterovalent isomorphous substitution schemes are possible in the fluorapatite structure type: $Ca^{2+} \leftrightarrow REE^{3+}$ and $(PO_4)^{3-} \leftrightarrow (SiO_4)^{4-}$; they determine three possible fluorine-dominant mineral species in the system: 1. fluorapatite (Ca- and P-dominant), ideally $Ca_5(PO_4)_3F$; 2. fluorbritholite-(REE) (REE- and Si-dominant), ideally $Ca_2REE_3(SiO_4)_3F$; 3. fluorcalciobritholite (Ca- and Si-dominant), ideally $Ca_3REE_2(SiO_4)_2(PO_4)F$. 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 fluorcalciobritholite (Ca = ΣREE): $Ca_{2.5}REE_{2.5}(SiO_4)_{2.5}(PO_4)_{0.5}F$; 2) a limit between fluorcalciobritholite and fluorapatite (Si = P): $Ca_{3.5}REE_{1.5}(SiO_4)_{1.5}(PO_4)_{1.5}F$.

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 $Ca_{2.5}REE_2Th_{0.5}(SiO_4)_3F$, shows the possible existence of a P-free variety of fluorcalciobritholite, if the content of tetravalent cations is high. In general, we can argue a solid solution series between fluorcalciobritholite and the hypothetic phase $Ca_{3.5}(Th,U)_{1.5}(SiO_4)_3F$. The latter can be con-

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

Site	Site occupancy factors	x	y	z	U_{eq}
T	$Si_{0.325(2)}P_{0.175(2)}$	0.3718(3)	0.4001(3)	0.25	0.0261(6)
M(1)	$Ca_{0.218(2)}Ce_{0.115(2)}$	0.33333	0.66667	0.0006(2)	0.0311(4)
M(2)	$Ca_{0.283(4)}Ce_{0.217(4)}$	0.2487(1)	0.0107(1)	0.25	0.0330(3)
O(1)	$O_{0.5}$	0.4677(8)	0.5906(8)	0.25	0.043(2)
O(2)	$O_{0.5}$	0.4866(8)	0.3255(9)	0.25	0.037(2)
O(3)	$O_{1.0}$	0.2563(6)	0.3432(8)	0.4310(7)	0.054(2)
F	$F_{0.16667}$	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 fluorcalciobritholite.

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	Fluorcalciobritholite	Fluorbritholite-(Ce)	Fluorellestadite	Fluorapatite
Formula	$(Ca,REE)_5[(Si,P)O_4]_3F$	$(REE,Ca)_5[(Si,P)O_4]_3F$	$Ca_{10}(SO_4)_3(SiO_4)_3F_2$*	$Ca_5(PO_4)_3F$
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
ω	1.735	1.792	1.638	1.631 – 1.650
ε	1.730	1.786	1.632	1.627 – 1.646
Optical sign	(-)	(-)	(-)	(-)
Reference	this work	Gu *et al.*, 1994	Chesnokov *et al.*, 1987	Anthony *et al.*, 2000

* – the empirical formula of the holotype specimen of fluorellestadite from Kopeisk, South Urals, Russia, is:
$(Ca_{9.97}Mn_{0.03})_{\Sigma10.00}[(SO_4)_{2.84}(SiO_4)_{2.79}(PO_4)_{0.20}(CO_3)_{0.17}]_{\Sigma6.00}F_{2.08}O_{0.07}$ (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 hydroxylellestadite, $Ca_{10}(SO_4)_3(SiO_4)_3(OH)_2$, 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 $Ca_{3.5}(Th,U)_{1.5}(SiO_4)_3(OH)$ reported by Jamtveit *et al.* (1997) in alkaline-calcareous metamorphic rocks from the Oslo Rift, Southern Norway, which forms a solid solution series with hydroxylbritholite-(Ce).

It is also not excluded that the *X* position in britholites – calciobritholites can be partially occupied by O^{2-} and/or vacant. This assumption is based on the existence of some synthetic apatite-type compounds in the system Ca–*REE*–Si–P,

namely $Ca_6La_4(SiO_4)_4(PO_4)_2O\square$, $Ca_4La_6(SiO_4)_6O\square$ (Boyer *et al.*, 1997), $Ca_6La_2Ce_2(SiO_4)_6$ (Cockbain & Smith, 1967), $Ca_6La_4(SiO_4)_2(PO_4)_4O_2$, $Ca_2La_8(SiO_4)_6O_2$ (Ito, 1968), and some others (*e.g.*, with other *REE*). The latter compound can be considered as the synthetic analogue of a hypothetic "oxybritholite" end-member, and the compound $Ca_6REE_4(SiO_4)_6$ is the synthetic analogue of a hypothetic *X*-vacant calciobritholite end-member. The compound $Ca_6REE_4(SiO_4)_2(PO_4)_4O_2$ can be considered as a *REE*,Si-

bearing "oxyapatite". Note that a significant incorporation of the "oxybritholite" component could takes 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 fluorcalciobritholite contains 0.25 O *apfu*.

Thus, in the "simplified" system (*i.e.*, without the substitutions involving tetravalent cations Th and U, and O^{2-} and vacancy in the *X* position), the fluorapatite composition field falls within the limits of $Ca_5(PO_4)_3F$ – $Ca_{3.5}REE_{1.5}(SiO_4)_{1.5}(PO_4)_{1.5}F$, and the fluorbritholite-(REE) field falls within the limits of $REE_3Ca_2(SiO_4)_3F$ – $Ca_{2.5}REE_{2.5}(SiO_4)_{2.5}(PO_4)_{0.5}F$. The fluorcalciobritholite field lies within the limits $Ca_{2.5}REE_{2.5}(SiO_4)_{2.5}(PO_4)_{0.5}F$ – $Ca_{3.5}REE_{1.5}(SiO_4)_{1.5}(PO_4)_{1.5}F$; the formula of idealized ("mid-member") fluorcalciobritholite is considered as $Ca_3REE_2(SiO_4)_2(PO_4)F$. Its La-dominant analogue, $Ca_3La_2(SiO_4)_2(PO_4)F$, (space group $P6_3/m$) 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^{2-} at the *X* position, in place of monovalent anions (F^-, OH^-, Cl^-). Theoretically, also the substitution mechanism $Ca^{2+} \leftrightarrow (Na,K)^+$ could play some role in obtaining balanced formulae, but its extent in natural britholites seems definitely minor.

The simplified structural formula of fluorcalciobritholite is $(Ca,REE)_2(Ca,REE)_3[(Si,P)O_4]_3F$, whereas in hydroxylbritholite-(Ce) and hydroxylbritholite-(Y) REE prevail over Ca at both independent larger cation sites: $(REE,Ca)_2(REE,Ca)_3[(Si,P)O_4]_3(OH,F)$, (Genkina *et al.*, 1991; Noe *et al.*, 1993) or at either: $(Ca,REE)_2(REE,Ca)_3[(Si,P)O_4]_3(OH,F)$ (Noe *et al.*, 1993).

The relationship of apatite with other related Si-bearing Ca-dominant mineral species, namely ellestadites, $Ca_5(SO_4)_{1.5}(SiO_4)_{1.5}X$, ($X = OH^-$, Cl^-, F^-), is characterized by another isomorphous substitution scheme: $2(PO_4)^{3-} \leftrightarrow (SiO_4)^{4-} + (SO_4)^{2-}$. 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 $(SO_4)/(SiO_4)$ ratio close to 1. Note that almost all of the known analyses of natural ellestadites, including the only published quantitative analysis of fluorellestadite, $Ca_5(SO_4)_{1.5}(SiO_4)_{1.5}F$, 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 fluorcalciobritholite. 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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