BYZANTIEVITE,
$Ba_5(Ca,REE,Y)_{22}(Ti,Nb)_{18}(SiO_4)_4[(PO_4),(SiO_4)]_4(BO_3)_9O_{21}[(OH),F]_{43}(H_2O)_{1.5}$,
A NEW MINERAL[1]

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A new silico-phosphate of Ba, Ca, *REE*, Ti, and Nb found in the Darai-Pioz alkaline massif, Tajikistan, has been named byzantievite because of its complex chemical composition and structure, reminiscent of the complex, but well-organized structure of the Byzantine Empire. The new mineral was discovered on a rock composed of microcline, quartz, aegirine and ferrileakeite; accessory minerals are: calcybeborosilite-(Y), pyrophanite, stillwellite-(Ce), danburite, thorite and pyrochlore. The new mineral occurs as tabular grains up to 0.5 x 1.8 mm in size and aggregates of these grains up to 2.5 mm in size. Byzantievite is brown with a pale-yellow streak. Luster is vitreous, slightly greasy on fracture surfaces. Cleavage is not observable; fracture is conchoidal. The Mohs' hardness is $4.5 - 5$. The mean (10 measurements) microhardness VHN is 486 kg/mm^2. The measured density is 4.10(3) g/cm^3, calculated density is 4.15 g/cm^3. Byzantievite is optically negative, uniaxial, $\omega = 1.940$, $\varepsilon = 1.860 \pm 0.005$. The new mineral is pleochroic from light brown along ε to very pale brown along ω; absorption is $\varepsilon \gg \omega$. The symmetry is hexagonal, space group $R3$, $a = 9.128(5)$; $c = 102.1(1)$ Å; $V = 7363$ (15) Å^3, Z = 3. The crystal structure was solved to $R_1 = 13.14\%$. The strong reflections in the X-ray powder — diffraction pattern are (d, Å; I; hkl): 4.02(2)(-1 2 12); 3.95(2)(-222); 3.112(10)(1 1 24; -1 2 24); 2.982(4)(-321; -231); 2.908(2)(1 1 27; -138; 128); 2.885(2)(-3 2 10; -2 3 10); 2.632(2)(030); 2.127(2)(0 0 48). The chemical composition is as follows (electron microprobe, average value and range of content of 60 point analyses; B$_2$O$_3$ was determined by SIMS; H$_2$O on the basis of structural data; wt.%): SiO$_2$ 4.73(3.15 − 5.84), Nb$_2$O$_5$ 10.97 (10.35 − 12.82), P$_2$O$_5$ 3.83(2.64 − 4.88), TiO$_2$ 15.21(13.84 − 16.56), ThO$_2$ 1.48(1.48 − 1.88), UO$_2$ 0.55(0.29 − 0.35), La$_2$O$_3$ 4.01(3.27 − 4.41), Ce$_2$O$_3$ 9.19(6.76 − 9.73), Nd$_2$O$_3$ 3.35(3.42 − 4.42), Pr$_2$O$_3$ 1.02(0.17 − 1.77), Sm$_2$O$_3$ 0.71 (0.58 − 1.23), Dy$_2$O$_3$ 1.25(1.05 − 1.30), Gd$_2$O$_3$ 0.95(0.68 − 1.49), Y$_2$O$_3$ 7.39(5.21 − 9.00), B$_2$O$_3$ 5.09(4.38 − 6.12), FeO 0.49(0.48 − 0.73), BaO 13.30(12.76 − 14.91), CaO 8.01(5.41 − 10.31), SrO 1.95(1.08 − 2.17), Na$_2$O 0.16 (0.00 − 0.22), H$_2$O 6.00, F 1.80(1.30 − 2.08), O = F (-0.76), total is 100.68. The empirical formula, calculated on the basis of 124.5 anions for the grain used for the structure analysis is: $Ba_{5.05}[(Ca_{8.99}Sr_{0.96}Fe^{2+}_{0.42}Na_{0.10})_{\Sigma10.47}(Ce_{3.46}La_{1.54}Nd_{1.20}Pr_{0.30}Sm_{0.26}Dy_{0.41}Gd_{0.32}Th_{0.39}U^{4+}_{0.17})_{\Sigma8.03}Y_{3.53}](Ti_{12.31}Nb_{5.30})_{\Sigma17.61}(SiO_4)_{4.65}(PO_4)_{3.12}(BO_3)_{8.89}O_{22.16}(OH)_{38.21}F_{4.89}(H_2O)_{1.5}$. The simplified formula is $Ba_5(Ca,REE,Y)_{22}(Ti,Nb)_{18}(SiO_4)_4[(PO_4),(SiO_4)]_4(BO_3)_9O_{21}[(OH),F]_{43}(H_2O)_{1.5}$. The compatibility index 0.003 (from calculated density) and -0.009 (from measured density). The type material was deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia.
4 figures, 3 tables, 18 references.
Keywords: byzantievite, silico-phospho-borate of Ba, Ca, *REE*, Ti, Nb, new mineral, Darai-Pioz, Tajikistan, alkaline rocks.

A new silico-pospho-borate mineral with an extremely complex composition and simplified formula $Ba_5(Ca,REE,Y)_{22}(Ti,Nb)_{18}(SiO_4)_4[(PO_4),(SiO_4)]_4(BO_3)_9O_{21}[(OH),F]_{43}(H_2O)_{1.5}$ was discovered in the Darai-Pioz massif, Tajikistan. To reflect the complexity and chemical diversity of the structure of this mineral, we have named it byzantievite. From nearly twelve centuries (374 − 1453), the Byzantine Empire was home to many nations and religions. The structure of the Byzantine Empire was very complex, but nevertheless, this state was well-organized, effective and had a major influence on European and World culture.

Occurrence

Byzantievite was discovered from one specimen collected from the moraine of the Darai-Pioz glacier, Tajikistan (N 39°27', E 70°43'). The

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valley of the glacier cuts the multiphase igneous complex of the same name, whose marginal zone of tourmalinized granite of Late Carboniferous age changes toward the center to biotite granite of Late Carboniferous to Early Permian age; the central part comprises quartz and quartz-free aegirine syenite of Permian age. A stock of Upper Permian to Middle Triassic cancrinite foyaite occurs in the southeastern massif. All listed igneous rocks are cut by Early to Middle Triassic fine-grained granite (Dusmatov, 1971). Pegmatites, hydrothermal rocks and carbonatites variable in composition and age and containing extensive REE, B, Li, Cs, Zr, Ti, Nb, and Ba mineralization are abundant in the massif (Dusmatov and Mogarovsky, 1971; Maiorov and Gavrilin, 1971).

Unfortunately, most of the massif is covered by the glacier or is hard-to-reach rock outcrops, strongly hampering investigation. Therefore, most mineralogical and petrographic data for the massif have been obtained on glacier debris.

The first data on the Darai-Pioz massif are related to the 1932−1936 Tajik-Pamir Expedition (Moskvin, 1937). Since then, many researchers have studied this massif. Vyacheslav Dzhuraevich Dusmatov contributed substantially to the mineralogical study of Darai-Pioz and his doctoral thesis is a thorough review of the geology and petrography of this massif (Dusmatov, 1971). The mineralogy, geochemistry and petrography of the massif are discussed in many papers (Dusmatov, 1968_1, 1968_2; Semenov and Dusmatov, 1975; Efimov, 1983; Vladykin and Dusmatov, 1996; Mogarovsky, 1987; Pekov et al., 2000; Belakovskiy, 1991; Grew et al., 1993; Reguir et al., 1999).

The Darai-Pioz massif is characterized by a high boron content. According to Dusmatov et al. (1972), the average boron content in the rocks of the massif is (ppm): 900 in tourmalinized granite, 74 in fine-grained biotite granite, 130 in porphyry granite, 53 in quartz syenite, 75 in aegirine syenite, 415 in alkaline pegmatite, and 60 in albitite. Currently, twenty four boron minerals with dominant boron at one structural site have been found in the massif. Nine new minerals have been discovered at this massif: byzantievite, calcybeborosilite-(Y), kapitsaite-(Y), kirchhoffite, maleevite, pekovite, tadzhikite-(Ce), tadzhikite-(Y), and tienshanite. It is of interest that eight boron minerals found at Darai-Pioz contain REE (including Y) as species forming elements and eight minerals contain Ba. Moreover, the mutual occurrence of boron with REE, Y, and Ba (as in byzantievite) is extremely characteristic feature of the minerals from this massif. The importance of boron in the Darai-Pioz massif is exhibited not only as elevated boron content and mineral diversity, but also as unique rocks, in which reedmergnerite, $NaBSi_3O_8$, a boron analogue of albite, is the major rock-forming mineral (Dusmatov et al., 1967). Leucosphenite, stillwellite-(Ce), and danburite are typical accessory minerals of certain pegmatites in this massif; calcybeborosilite-(Y) is typical of fenitized rocks. The diversity of phosphorous minerals in the massif is more modest; currently, only three minerals containing phosphorous as an essential element are known here: fluorapatite (abundant in variable rock types) monazite-(Ce) (sporadical findings), and byzantievite.

Byzantievite was found in a coarse-grained rock composed mainly of approximately equal amounts of microcline, quartz, aegirine and ferrileakeite. Microcline occurs as white (with a weak yellowish-green tint) coarse anhedral grains (up to 3 cm across) with well-developed perthite ingrowths of albite. Quartz occurs as semitransparent slightly smoky grains ranging from 0.5 to 2 cm in size. Aegirine is present as euhedral crystals (up to $4 \times 6 \times 15$ mm) and dark grass-green aggregates of these grains are randomly distributed in quartz-microcline. Ferrileakeite occurs as long dark grains and aggregates up to 2 cm in length, frequently intergrown with pyroxene. Titanite, nalivkinite and zircon are minor phases. Accessory minerals are calcybeborosilite-(Y), pyrophanite, stillwellite-(Y), danburite, thorite, pyrochlore and byzantievite. The composition of selected minerals from this described assemblage is given in Table 1.

Byzantievite occurs as intergrowths (up to 2.5 mm in size) of tabular grains (Fig. 1) in quartz and microcline, frequently intergrown with aegirine, zircon, thorite, calcybeborosilite-(Y) and pyrophanite.

Physical properties

Byzantievite occurs as lamellar and tabular grains flattened parallel on {001} with poorly-formed faces reaching 0.5×1.8 mm in size, and as aggregates of grains. Nearly all grains are deformed to some extent; fractures are healed by quartz and calcybeborosilite-(Y) that hampers separation of pure material for examination. The mineral is brown with a pale-yellow streak. Luster is vitreous and slightly greasy on fracture surfaces. Byzantievite is semitransparent and transparent in small flakes. Cleavage is not observed; the fracture is conchoidal. The Mohs' hardness is 4.5−5. Microhardness (VHN) measured with PMT-3 (calibrated with NaCl) with loading 50 g is 486 (average of 10 measurements ranging from 463 to 522) kg/mm^2. The
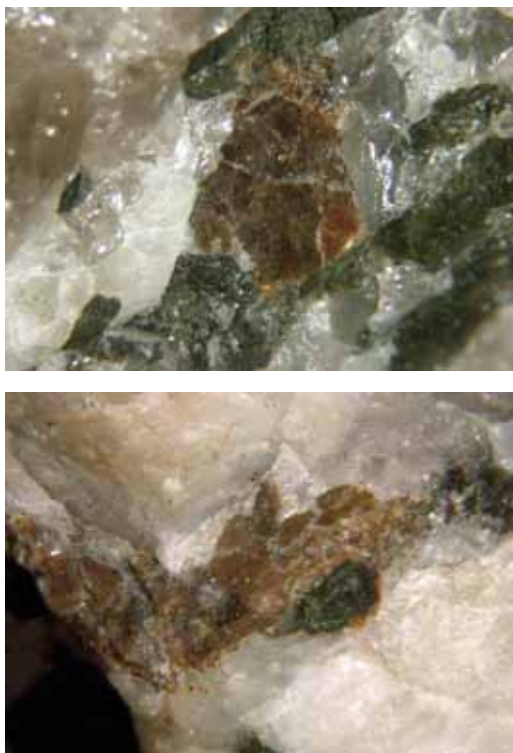
Fig. 1. Segregations of byzantievite and associated minerals: (a) lamellar brown byzantievite in an aegirine-quartz-microcline matrix; (b) aggregate of byzantievite, calcybeborosilite-(Y), zircon, and aegirine in microcline. Oblique light. Width of image is 6 mm.

Table 1. Chemical composition (wt.%) of minerals associated with byzantievit

Component	1	2	3	4	5	6	7
SiO$_2$	52.39	51.88	29.63	27.16		35.29	22.45
TiO$_2$	0.89	0.42	37.54	0.15	53.32	11.28	14.97
SnO$_2$	n.a.		0.18			0.17	
ZrO$_2$						0.13	0.37
Nb$_2$O$_5$			1.94		0.57	0.43	0.20
Al$_2$O$_3$	0.57	0.39	0.12			1.06	0.17
Fe$_2$O$_3$	*16.96	32.76					
FeO	*10.38		0.97	5.82	15.52	22.35	14.85
MnO	1.68	0.57		0.28	31.37	12.28	12.12
MgO	2.57	0.19				0.65	0.10
ZnO	0.38	0.05				0.43	0.38
CaO	0.37	2.22	24.30	12.09		2.30	
BaO	n.a.	n.a.		0.15			29.60
Na$_2$O	7.80	11.73	1.54			1.33	
K$_2$O	2.09					2.49	
Li$_2$O	1.18	0.17	n.a.	n.a.	n.a.	1.23	n.a.
Cs$_2$O						2.46	
H$_2$O	1.12	n.a.	n.a.	n.a.	n.a.	2.88	2.08
F	1.98	n.a.	1.23	n.a.	n.a.	1.49	3.50
-O=F	0.83	-	0.52	-		0.63	1.47
Total	99.53	100.34	98.16	79.28	100.77	97.62	99.32

Notes: n.a. denotes that the component was not analyzed; an empty cell denotes that the content of the component is below detection limit. Li zwas determined from a microsample by emission flame spectrophotometry, FMD 4 spectrometer; the content of H$_2$O is calculated.

(1) Ferrileakeite (dark green nearly black) (average of 5 point analyses), Camebax microbeam, 15 kV, 20 nA, ZAF; fluorine content was corrected with the PAP procedure:

*(Na$_{0.35}$K$_{0.40}$)$_{0.75}$(Na$_{1.94}$Ca$_{0.06}$)$_{2.00}$ (Fe$^{+2}_{1.31}$Mg$_{0.58}$ Mn$_{0.22}$ Zn$_{0.04}$)$_{2.15}$(Fe$^{+3}_{1.93}$Ti$_{0.10}$)$_{2.03}$Li$_{0.72}$(Si$_{7.92}$Al$_{0.10}$)O$_{22}$ (OH$_{1.05}$F$_{0.95}$)$_{2.00}$ (the formula is calculated with the WinAmphcal program on the basis of 23 O atoms (taking into account (F+OH) = 2); *Fe^{+2} and Fe^{+3} are calculated from average normalization between (Si+Al+Mg+Ti+Mn+Fe+Zn+Li) = 13 atoms and (Si+Al+Mg+Ti+Mn+Fe+Zn+Li+Ca+Na) = 15 atoms (Yavuz, 2007);*

(2) Aegirine (green), Camebax microbeam, 15 kV, 20 nA, ZAF: (Na$_{0.88}$Ca$_{0.09}$Li$_{0.03}$)$_{1.00}$(Fe$^{+3}_{0.94}$ Mn$_{0.02}$ Mg$_{0.01}$Ti$_{0.01}$)$_{0.98}$(Si$_{1.98}$Al$_{0.02}$)$_{2.00}$O$_6$ (calculated on the basis of 6 O atoms);

(3) Titanite (average of 11 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, fluorine was measured at 10 kV, 55 nA, TAP crystal, corrected with the PAP procedure. Total also includes (wt. %): 0.78 Ce$_2$O$_3$, 0.45 Nd$_2$O$_3$.

(Ca$_{0.88}$Na$_{0.10}$)$_{0.98}$(Ti$_{0.95}$Nb$_{0.03}$Fe$_{0.03}$Ce$_{0.01}$Nd$_{0.01}$)$_{1.03}$Si$_{1.00}$O$_{4.89}$F$_{0.13}$ (calculated on the basis of 3 cations);

(4) Calcybeborosilite-(Y), JEOL Superprobe 733, INCA, 20 kV, 2 nA. Total also includes (wt. %): Y$_2$O$_3$ 14.60; La$_2$O$_3$ 1.20, Ce$_2$O$_3$ 4.48, Pr$_2$O$_3$ 0.45, Nd$_2$O$_3$ 2.61, Sm$_2$O$_3$ 0.62, Gd$_2$O$_3$ 1.18, Dy$_2$O$_3$ 2.59, Ho$_2$O$_3$ 0.12, Er$_2$O$_3$ 1.38, Yb$_2$O$_3$; 0.56; UO$_2$ 1.17 ThO$_2$ 1.97; SrO 0.70; B and Be were not measured;

(5) Pyrophanite (average of 2 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, (Mn$_{0.67}$Fe$_{0.33}$)$_{1.00}$(Ti$_{1.00}$Nb$_{0.01}$)$_{1.01}$O$_3$ (calculated on the basis of 3 O atoms);

(6) Nalivkinite (average of 10 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, fluorine content was measured at 10 kV, 55 nA, TAP crystal, calculation with PAP procedure (Li$_{1.09}$K$_{0.70}$Cs$_{0.23}$)$_{1.02}$(Na$_{0.57}$Ca$_{0.54}$)$_{1.11}$(Fe$_{4.12}$Mn$_{2.29}$Mg$_{0.21}$Zn$_{0.07}$)$_{6.69}$(Ti$_{1.88}$Nb$_{0.04}$Zr$_{0.01}$Sn$_{0.01}$)$_{1.94}$ (Si$_{7.78}$Al$_{0.28}$)$_{8.06}$O$_{24}$((OH)$_{4.12}$F$_{1.04}$O$_{1.84}$)$_{7.00}$ (calculated on the basis of Σ(Si, Al, Ti, Nb, Sn, Zr) = 10 atoms; O and OH are calculated from charge balance);

(7) Bafertisite (average of 3 point analyses), JEOL Superprobe 733, INCA, 20 kV, 2 nA, fluorine content was measured at 10 kV, 55 nA, TAP crystal, calculation with PAP procedure Ba$_{1.01}$(Fe$_{1.08}$Mn$_{0.89}$Zn$_{0.02}$Mg$_{0.01}$)$_{2.00}$(Ti$_{0.98}$Zr$_{0.02}$Nb$_{0.01}$)$_{1.01}$(Si$_{1.96}$Al$_{0.02}$)$_{1.98}$ O$_8$(OH$_{0.98}$F$_{0.96}$)$_{1.97}$ (calculated on the basis of 6 cations; OH calculated from charge balance). Analyst L.A. Pautov.

density of byzantievite determined by flotation in Clerici solution is 4.10(3) g/cm^3; the calculated density is 4.15 g/cm^3.

The mineral is optically negative. The refractive indices, measured by the immersion method on spindle stage are (589 nm): ω = 1.940, ε = 1.860 ± 0.005. Byzantievite is strongly pleochroic from light brown along ε to very pale brownish along ω; absorption is ε >> ω.

Byzantievite is luminescent neither short nor longwave UV range (240 − 400 nm).

IR spectra were measured with Avatar (Thermo Nicolet) and Specord-75IR spectrophotometers in KBr disks. However, due to ingrowths of different phases in byzantievite, sufficient material to measure a good IR spectra could not be obtained. In the recorded IR spectra of the mineral, the strongest absorption is in the region 500 − 700 cm^{-1}, a broad band with three major peaks at 550, 590, 650 cm^{-1} due to superimposed bands of Si-O and P-O bending vibrations and M-O stretching vibrations, where M is Ca, Y, REE. The narrow band at 740 cm^{-1} most likely corresponds to Ti-O stretching vibrations; the broad

band with peaks at 950 and 1000 cm^{-1} is assigned to Si-O stretching vibrations. The narrow strong bands with maxima at 1190 and 1270 cm^{-1} correspond to P-O and B-O stretching vibrations, respectively.

According to the Gladstone-Dale relation, the compatibility index is superior: $1-K_P/K_C = 0.003$ using $D_{calc} = 4.15$ g/cm^3 and $1-K_P/K_C = -0.009$ using $D_{meas} = 4.10$ g/cm^3.

Chemical composition

Химический состав византиевитаду Si The chemical composition of byzantievite was measured with an electron microprobe. It was not possible to separate sufficient material to determine the H_2O concentration directly, and the H_2O content was calculated on the basis of the crystal structure. As the composition of the new mineral is extremely complex, it was determined in three laboratories (A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow; Department of Geological Sciences, University of Manitoba, Winnipeg, Canada; Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements, Moscow) with energy- and wavelength-dispersion methods. Seventy point analyses were obtained for nine grains (Table 2). The BSE image shows darker areas (with lower mean atomic number) related to fractures in some grains of byzantievite (Fig. 2). Examination of these areas show that they contain the same elements in similar ratios as normal byzantievite and most likely are caused by greater metamictization and probable hydration of the new mineral. We tried to avoid such altered areas during analysis, but it is possible, that this altered material was sometimes present in the zone of X-

Table 2. **Chemical composition (wt.%) of byzantievite**

Compo- nent	1 Average	1 Range of content	2 Average	2 Range of content	3 Average	3 Range of content	4 Semiquantitative data of ICP OES
SiO_2	4.52	4.19−5.80	4.73	3.15−5.84	3.82	3.74−3.99	n.a.
Nb_2O_5	11.38	10.43−12.17	10.97	10.35−12.82	13.32	11.90−13.83	>4
P_2O_5	3.58	2.99−3.87	3.83	2.64−4.88	3.97	3.69−4.29	>2
TiO_2	15.90	15.36−16.47	15.21	13.84−16.56	15.37	14.38−15.92	>9
ThO_2	1.65	1.39−1.84	1.48	1.48−1.88	1.30	1.11−1.50	1.4
UO_2	0.74	0.36−0.76	0.55	0.29−0.35	n.a.		0.3
La_2O_3	4.06	3.78−4.45	4.01	3.27−4.41	3.88	3.72−4.04	3.3
Ce_2O_3	9.17	8.53−10.22	9.19	6.76−9.73	8.11	7.63−8.61	8.1
Nd_2O_3	3.26	2.96−3.48	3.35	3.42−4.42	3.09	2.87−3.28	2.6
Pr_2O_3	0.79	0.37−1.21	1.02	0.17−1.77	n.a.		0.8
Sm_2O_3	0.73	0.58−0.84	0.71	0.58−1.23	0.54	0.30−0.73	0.8
Dy_2O_3	1.22	0.93−1.61	1.25	1.05−1.30	0.79	0.64−1.00	1.2
Gd_2O_3	0.93	0.68−1.23	0.95	0.68−1.49	0.77	0.69−0.93	0.9
Y_2O_3	6.44	6.14−6.85	7.39	5.21−9.00	6.33	5.84−8.00	6.1
B_2O_3	5.00		5.09	4.38−6.12	4.52	4.26−4.77	>1
FeO	0.49	0.29−0.59	0.49	0.48−0.73	n.a.		1.2
BaO	12.51	12.25−12.93	13.30	12.76−14.91	12.25	11.90−12.75	13.0
CaO	8.15	7.72−8.57	8.01	5.41−10.31	8.81	8.71−8.89	8.2
SrO	1.61	1.45−1.77	1.95	1.08−2.17	1.74	1.57−1.91	1.7
Na_2O	0.10	0.06−0.16	0.16	0.00−0.22	n.a.		0.5
$H_2O^\bullet$	6.00		6.00		n.a.		
F	1.50		1.80	1.30−2.08	n.a.		
-O=F	0.63		0.76				
Total	99.10		100.68				

Notes: n.a. denotes that the component is not analyzed; empty cell denotes that the content of the component is below detection limit.
(1) Average and range of content of 10 point analyses of the grain that was used to determine the crystal structure of the mineral. Cameca SX-100 operated at 15 kV, 10 nA, beam diameter 10 microns Standards are: fluorphlogopite (F), albite (Na), barite (Ba), $Ba_2NaNb_5O_{15}$ (Nb), diopside (Si, Ca), fayalite (Fe), titanite (Ti), apatite (P): ThO_2 (Th), UO_2 (U), LaPO_4 (La), CePO_4 (Ce), NdPO_4 (Nd), PrPO_4 (Pr), SmPO_4 (Sm); DyPO_4 (Dy), GdPO_4 (Gd), and YAG (Y). Data were corrected with the PAP procedure. Analyst Panseok Yang. B_2O_3 was measured with SIMS, Cameca IMS 4F, analyst S.G. Simakin; $H_2O^\bullet$ calculated from the structural data.
(2) Average and range of content of 60 point analyses of six grains; 11 compositions were measured with a JXA-50A scanning electron microscope equipped with a Link spectrometer operated at 20 kV, 2 nA, beam diameter 1 micron; 6 compositions were measured by WDS with a Camebax-microbeam electron microprobe operated at 15 kV, 20 nA, beam diameter 5 microns, fluorine was measured at 10 kV, 20 nA; 43 compositions were measured with a JCXA-733 scanning electron microscope equipped with an INCA EDS operated at 20 kV, 2 nA, beam diameter 1 micron, B_2O_3 was measured with JCXA-733, STE crystal, acceleration voltage 10 kV, current 100 нА, beam diameter 20 microns; standard is stillwellite-(Ce). Content was calculated with PAP procedure. Analyst L.A. Pautov;
(3) Average and range of content of 7 point analyses of one grain. Camebax-microbeam electron microprobe operated at 15 kV, 15 nA, beam diameter 5 microns. Standards are: [Стандарты] LiNbO_3 (Nb), Ba glass (Ba), Y_2SiO_5 (Si, Y), ilmenite (Fe, Ti), apatite (P), thorite (Th), light blue diopside (Ca), Sr glass (Sr), KLa(MoO_4)_2 (La); LiCe(WO_4)_2 (Ce), LiNd(MoO_4)_2, (Nd), LiSm(MoO_4)_2 (Sm), LiDy(WO_4)_2 (Dy), and LiGd(MoO_4)_2 Gd. B_2O3 was measured at 10 kV, 20 nA, beam diameter 5 microns. Standard is boron nitride. Content was calculated with PAP procedure. Analyst I.M. Kulikova.
(4) Composition of one grain after acid decomposition determined with ICP OES (Vista PRO, VARIAN), in addition, it was determined (wt. %):Al_2O_3 − 0.06; BeO − 0.09; Cr_2O_3 − 0.05; Er_2O_3 − 0.5; Eu_2O_3 − 0.09; Ho_2O_3 − 0.2; Lu_2O_3 − 0.01; Tb_2O_3 − 0.2; Yb_2O_3 − 0.2; Sc_2O_3 − 0.003; MnO − 0.08; ZnO − 0.008; Li_2O − 0.05; ZrO_2 − 0.005. Analyst L.A. Pautov.
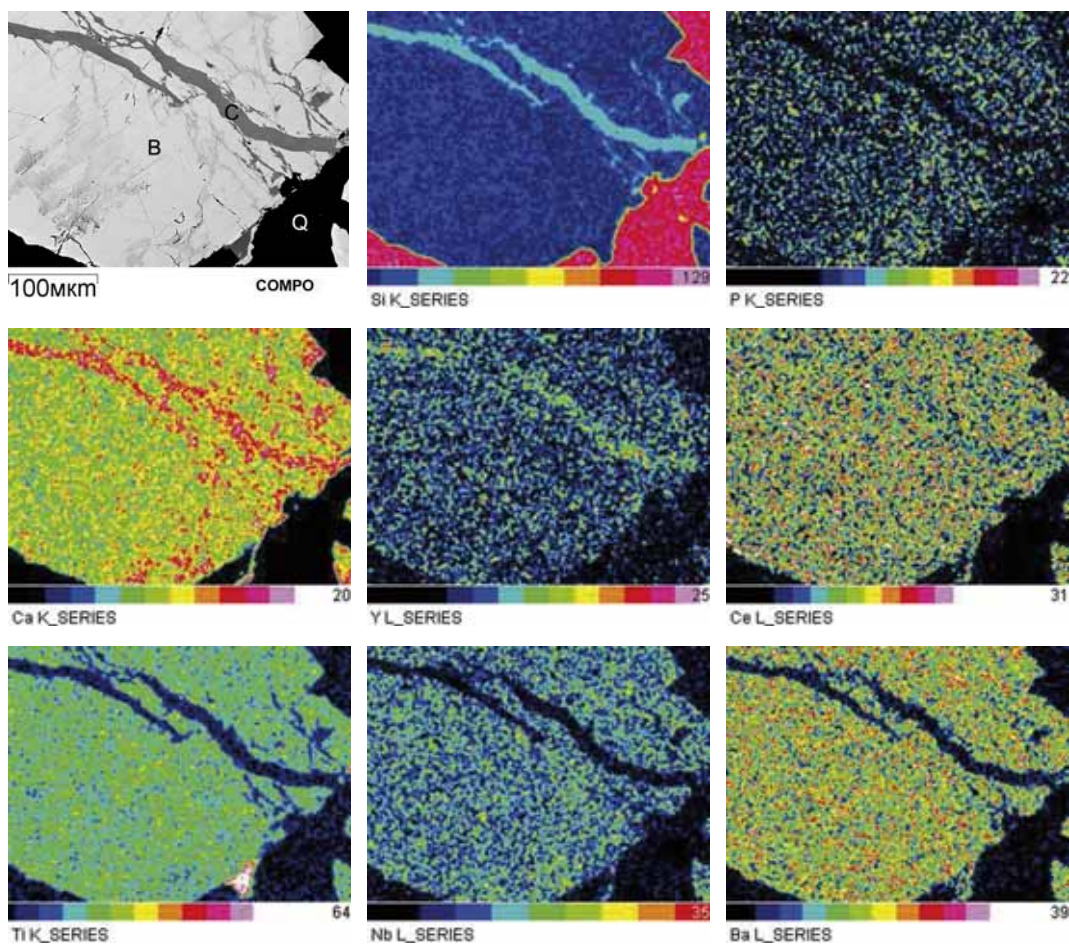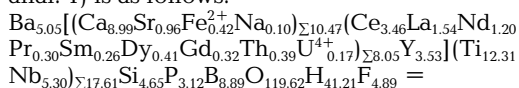
Fig. 2. Grain of byzantievite (B) with veinlet of calcybeborosilite-(Y) (C) in quartz (Q). COMPO image and X-ray distribution maps of elements.

ray generation. Significant variation in the measured chemical composition of byzantievite is probably caused not only by chemical substitution in the mineral, but also by such alteration. In variation diagrams (Fig. 3), this is a clear negative correlation between Ca and REE+Y, and between Si and P. There is not a well-developed correlation between Nb and Ta. This may be due to: inevitable analytical errors, altered areas in the mineral grains, and probable occupancy of a few sites by one element, and the presence of extensive vacancies. In our opinion, the latter is predominant factor here (Sokolova *et al.*, 2010).

The lithium and beryllium contents of byzantievite were measured with SIMS and ICP-OES. A fragment of the grain used for solution of the crystal structure (Table 2, anal. 1) was studied with a Cameca IMS-4F ion microprobe (analyst S.G. Simakin, Institute of Microelectronics and Informatics, Russian Academy of Sciences) oper-

ated at O$_2^-$ primary beam with an energy of 14.5 keV focused to the spot of 10−20 microns. The absolute concentration of each element, calculated from the element/^{30}Si$^+$ ratio of intensity of ion current using calibrated constants, are (wt.%): 0.07 Li$_2$O; 0.002 BeO. To analyze by ICP-OES, a grain of the new mineral (after checking the chemical composition with EDS) was dissolved and the intensities of the lines of determined elements were measured; the concentration of the elements was calculated by the ratio method (with reference to the element Ca).

The empirical formula calculated on the basis of 124.5 anions (O + F), for the grain used for the solution of the crystal structure (Table 2, anal. 1) is as follows:
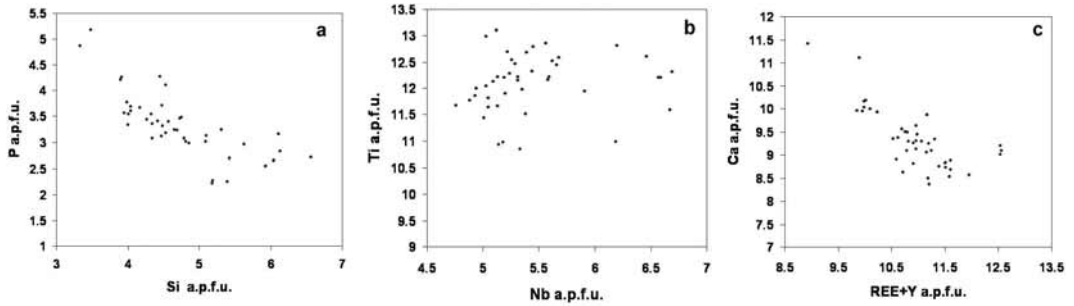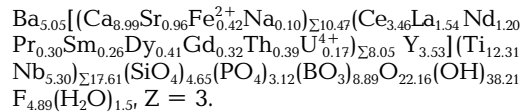Ba$_{5.05}$[(Ca$_{8.99}$Sr$_{0.96}$Fe$^{2+}_{0.42}$Na$_{0.10}$)$_{\Sigma 10.47}$(Ce$_{3.46}$La$_{1.54}$Nd$_{1.20}$Pr$_{0.30}$Sm$_{0.26}$Dy$_{0.41}$Gd$_{0.32}$Th$_{0.39}$U$^{4+}_{0.17}$)$_{\Sigma 8.05}$Y$_{3.53}$](Ti$_{12.31}$Nb$_{5.30}$)$_{\Sigma 17.61}$Si$_{4.65}$P$_{3.12}$B$_{8.89}$O$_{119.62}$H$_{41.21}$F$_{4.89}$ =

Fig. 3. P versus Si (a), Ti versus Nb (b), and Ca versus REE+Y (c) variation diagrams in atoms per formula unit of byzantievite.

Table 3. **X-ray powder-diffraction data of byzantievite**

I	d_{obs}	d_{calc}	hkl
1	4.56	4.560	-1 2 0
1	4.23	4.231	1 1 9
2	4.02	4.020	-1 2 12
2	3.95	3.937	-2 2 2
1	3.56	3.555	-1 2 18
			1 1 18
1	3.40	3.405	0 0 30
1	3.25	3.300	-2 2 17
		3.217	0 1 29
10	3.112	3.111	1 1 24
			-1 2 24
4	2.982	2.984	-3 2 1
			-2 3 1
1	2.931	2.925	-2 3 7
2	2.908	2.912	1 1 27
		2.907	-1 3 8
			1 2 8
2	2.885	2.865	-3 2 10
			-2 3 10
1	2.762	2.763	-1 3 14
			1 2 14
2	2.632	2.633	0 3 0
1	2.412	2.409	-1 2 36
			1 1 36
1	2.264	2.271	-1 2 39
			1 1 39
		2.260	-2 4 6
			2 2 6
1	2.201	2.202	-2 4 12
			2 2 12
2	2.127	2.128	0 0 48
1	1.928	1.928	-1 2 48
			1 1 48
>1	1.894	1.895	-2 4 30
			2 2 30
1	1.835	1.836	2 2 33
			-2 4 33
1	1.725	1.722	0 4 29
1	1.508	1.507	-3 6 9
			3 3 9
1	1.493	1.493	-2 6 1

Notes: Analyst L.A. Pautov.

$Ba_{5.05}[(Ca_{8.99}Sr_{0.96}Fe^{2+}_{0.42}Na_{0.10})_{\Sigma10.47}(Ce_{3.46}La_{1.54}Nd_{1.20}Pr_{0.30}Sm_{0.26}Dy_{0.41}Gd_{0.32}Th_{0.39}U^{4+}_{0.17})_{\Sigma8.05}\ Y_{3.53}](Ti_{12.31}Nb_{5.30})_{\Sigma17.61}(SiO_4)_{4.65}(PO_4)_{3.12}(BO_3)_{8.89}O_{22.16}(OH)_{38.21}F_{4.89}(H_2O)_{1.5}$, Z = 3.

E.V. Sokolova *et al.* (2010) suggested the simplified formula of byzantievite on the basis of cation groups determined by cation sites in the structure; in this case, vacancies were omitted to avoid an overly complicated formula: $Ba_5(Ca,REE,Y)_{22}(Ti,Nb)_{18}(SiO_4)_4[(PO_4),(SiO_4)]_4(BO_3)_9O_{21}[(OH),F]_{43}(H_2O)_{1.5}$, Z = 3. Note that in the empirical and simplified formulae, the number of "additional" oxygen atoms (i.e., not incorporated into silicate, phosphate, borate, and hydroxyl anions) is different: 22, 16 and 21, respectively, to the oxyanions introduced as integers in the idealized formula. The empirical and simplified formulae are written with different numbers of oxygen atoms in order to retain the number of anions per formula unit as 124.6; this is very important as the empirical formula of byzantievite was calculated on the basis of this fixed number of anions.

X–ray crystallography

The X-ray powder-diffraction pattern of byzantievite was recorded with an RKD-57.3 camera, Fe*K*α-radiation, and quartz as an internal standard. The X-ray powder-diffraction data are given in Table 3. The unit-cell dimensions calculated by the least-squares method on the basis of 16 reflections for hexagonal symmetry are: $a = 9.128(5)$; $c = 102.1(1)$ Å; $V = 7363(15)$ Å^3. The X-ray powder-diffraction pattern of byzantievite is unique and has no analogues among natural and synthetic compounds.

The crystal structure of byzantievite, hexagonal *R*-cell, space group *R3* and unit-cell dimensions: $a = 9.1202(2)$, $c = 102.145(5)$ Å, $V = 7358.0(5)$ Å^3, Z = 3, was solved with a single crystal by direct methods and refined to $R_1 = 13.14\%$ on the basis of 3794 reflections with $[F_o > 4\sigma|F|]$ from an experimental set of reflections measured

with MoKα-radiation on a Bruker *P4* diffractometer equipped with a CCD detector (Sokolova *et al.*, 2010). The crystal structure of byzantievite is a framework of polyhedra dominated by Ti, Ba, Ca, Y, and *REE* cations and SiO$_4$ and PO$_4$ tetrahedra, and BO$_3$ triangles. The independent part of the structure is shown in Fig. 4; the whole structure is constructed by repetition of the independent part by the R translation. Sixteen polyhedron layers parallel to (001) are distinguished in the independent part of the structure. Layers B, H, J, and P consist of (Ti,Nb) medium-sized polyhedra, and layers A and B-G are composed of large Ba and (Ca,REE) polyhedra. In the crystal structure, there are 50 cation sites which may be divided into three groups with occupancies of 100%, ~ 67%, and ~ 17%, respectively. The presence of three groups of cation sites allow us to distinguish three components in the structure of byzantievite: one fully ordered with 100% occupancy of cation sites, and two disordered with ~ 67% and ~ 17% occupancy of cation sites. We suggest that the latter two parts are linked by hydrogen bonds (Sokolova *et al.*, 2010).

The holotype sample of byzantievite has been deposited in the A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, registration number 3791/1.

Acknowledgements

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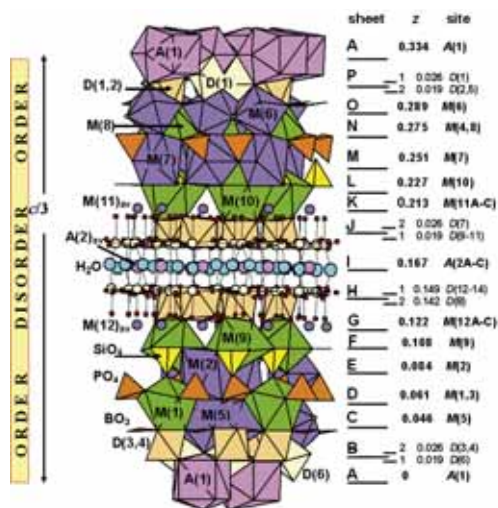*Dusmatov V.D.* Geochemistry and mineralogy of boron in alkaline rocks (South Tien-Shan).// II Respublicanskaya Nauchnaya Conferentsia Tajikskoi SSR. Abstracts. Dushanbe. **1968$_1$**. P.147−148 (in Russian).

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Fig. 4. General view of one third of the crystal structure of byzantievite parallel to [001]. (BO$_3$) triangles, (SiO$_4$) and (PO$_4$) tetrahedra are red, yellow and orange, respectively. Cation polyhedra are shown for cation sites occupied more than 50 %: [12]-fold Ba polyhedra are pink; [10]- and [8]-fold M polyhedra are green and violet; Ti octahedra are dark yellow [D(2-5,7,8)] and light yellow [D(1,6). Atoms at the sites occupied less than 50 % are depicted as spheres: A(2A-C) pink, D(9-14) pale yellow, M(11A-C) and M(12A-C) violet; triple sites A(2A-C), M(11A-C), and M(12A-C) are shown as one sphere: A(2)av, M(11)av, and M(12)av, where av = average. Fluorine atoms and OH groups are depicted as small yellow and red spheres; H$_2$O groups as large light blue spheres. Bonds D(9-14 − anions are shown as thin black lines. Sixteen polyhedron sheets parallel to (001) are depicted as horizontal black lines in the right part of this Figure (these sheets correspond to the 1/3 of the c parameter). Each sheet is characterized by the Z coordinate and cation sites, which compose this sheet. The sheets composed of Ti octahedra (B, H, J, and P) are divided into two subsheets, e.g. B$_1$ and B$_2$, where 1 and 2 correspond to light yellow and dark yellow octahedra.

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