# Popugaevaite, $Ca_3[B_5O_6(OH)_6]FCl_2 \cdot 8H_2O$, a new phylloborate mineral

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## Abstract

The new mineral popugaevaite $Ca_3[B_5O_6(OH)_6]FCl_2 \cdot 8H_2O$ was found at the Internatsional'nyi diamond mine, Internatsional'naya kimberlite pipe, Sakha (Yakutia) Republic, Russia. It belongs to the low-temperature hydrothermal mineral assemblage formed in the contact zone between

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kimberlite and a boron-bearing halite rock. Popugaevaite occurs as veinlets in massive aggregates of ekaterinite and crusts (up to 0.7 mm thick and up to 1 cm × 4 cm in area) on ekaterinite nodules embedded in halite. Other associated minerals are Fe-rich szaibélyite, serpentine, dolomite, pyrrhotite, and chalcopyrite. Crude prismatic crystals of popugaevaite are up to 0.3 × 1 mm. The mineral is transparent, colourless, with vitreous lustre and perfect {010} cleavage. It is optically biaxial (–), α 1.502(2), β 1.523(2), γ 1.530(2) and $2V_{meas}$ = 50(10)º. The chemical composition (wt.%, electron-microprobe, boron by ICP-MS, $H_2O$ calculated by stoichiometry) is: CaO 28.54, $B_2O_3$ 28.62, F 3.19, Cl 11.50, $H_2O$ 32.83, O=(F,Cl) –3.94, total 100.74. The empirical formula, calculated based on 23 O+F+Cl and 22 H atoms per formula unit, is $Ca_{3.07}B_{4.96}O_{6.03}(OH)_6F_{1.01}Cl_{1.96} \cdot 8H_2O$. Popugaevaite is monoclinic, space group $Pn$, $a$ 8.7055(11), $b$ 8.1025(11), $c$ 14.812(2) Å, β 91.367(7)°, $V$ 1044.5(2) Å$^3$ and $Z$ = 2. The strongest reflections of the powder XRD pattern [$d$,Å($I$,%)($hkl$)] are: 8.12(100)(010), 4.058(27)(020), 3.577(15)(–121), 2.936(10)(123), 2.834(16)(301, –105) and 2.283(10)(133). The crystal structure was solved based on single-crystal XRD data and refined on powder data by the Rietveld method, $R_{wp}$ = 0.0058, $R_p$ = 0.0043, $R_{obs}$ = 0.0241. Popugaevaite is an isostructural analogue of brianroulstonite $Ca_3[B_5O_6(OH)_6](OH)Cl_2 \cdot 8H_2O$ with F$^-$ instead of the OH$^-$ group non-bound with boron. The structure is based upon the layers of twelve-membered rings of alternating $BO_3$ triangles and $BO_2(OH)_2$ tetrahedra. The mineral is named in honour of the Russian geologist Larisa Anatol'evna Popugaeva (1923–1977), one of the principal discoverers of diamondiferous kimberlite pipes in Yakutia.

**Keywords:** popugaevaite; new mineral; brianroulstonite; hydrous calcium borate; fluoro-chloro-borate; crystal structure; Internatsional'naya kimberlite pipe.

## Introduction

In this paper, we describe the new mineral popugaevaite (Cyrillic: попугаеваит), the first natural borate with both F and Cl as species-defining constituents. It was found at the Internatsional'nyi diamond mine operated on the Internatsional'naya kimberlite pipe in Sakha (Yakutia) Republic, Russia. This kimberlite pipe, a well-known, actively operating diamond deposit, is the type locality of two recently discovered crichtonite-hroup minerals, botuobinskite $SrFe^{2+}Mg_2(Cr^{3+}_6Ti^{4+}_{12})[O_{36}(OH)_2]$ and mirnyite $SrZr^{4+}Mg_2(Cr^{3+}_6Ti^{4+}_{12})O_{38}$ (Rezvukhin *et al.*, 2023).

Popugaevaite was found in a single (holotype) specimen of a core of a prospecting borehole drilled from an underground working. It is named in honour of the Russian geologist Dr. Larisa Anatol'evna Popugaeva (1923–1977), one of the principal discoverers of diamondiferous kimberlite pipes in Yakutia. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification, IMA2019–115. The type specimen (a part of holotype) is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow with the catalogue number 97010.

## Occurrence and general appearance

The new mineral was found in the only specimen, a fragment of the core of a prospecting borehole drilled at the Internatsional'nyi (International) underground diamond mine, Internatsional'naya kimberlite pipe, Irelyakh river basin, 10 km SW of the city of Mirnyi, Sakha (Yakutia) Republic, Siberia, Russia.

The Internatsional'naya pipe breaks through the Early Cambrian sedimentary strata mainly consisting of terrigenous-carbonate, carbonate and evaporitic rocks. This sedimentary strata contains layers of halite rocks, from 1.5 m to 30 m thick, with accessory dolomite, anhydrite, celestine and the borate mineral kurgantaite $CaSr[B_5O_9]Cl \cdot H_2O$. Numerous xenoliths of halite rocks up to several meters in size, as well as veins of recrystallized halite and breccias with halite cement, are typical for the Internatsional'naya pipe, like some other Yakutian kimberlite pipes (Kopylova *et al.*, 2013; Agashev *et al.*, 2018 and references therein). An interesting geochemical and mineralogical feature of the Internatsional'naya pipe is the presence of a rich borate mineralization of the low-temperature hydrothermal origin in the contact zone between kimberlite and halite xenoliths and in halite veins. The major borate mineral here is ekaterinite $Ca_2(B_4O_7)(Cl,OH)_2 \cdot 2H_2O$ which forms numerous nodules and veins up to 4.5 cm thick, sometimes together with serpentine (Nikulin and Eremeev, 2011). In ekaterinite aggregates, halite and an unusually $Fe^{2+}$-enriched variety of szaibélyite (up to 28.5 wt.% FeO) form thin veinlets (Zubkova *et al.*, 2020).

Popugaevaite occurs as veinlets in massive, fine-grained aggregates of reddish-pink ekaterinite and crusts on ekaterinite nodules (Fig. 1) embedded in halite. Other associated minerals include Fe-enriched szaibélyite, serpentine, dolomite, pyrrhotite, and chalcopyrite. The veinlets and crusts of popugaevaite are typically 0.2–0.3 mm, rarely up to 0.7 mm in thickness and up to 1 cm × 4 cm in area. They consist of coarse prismatic, sometimes lath-shaped, typically split individuals (crude crystals: Fig. 2) up to 0.3 mm × 1 mm. Aggregates of the new mineral contain numerous inclusions of halite and Fe-bearing szaibélyite.

**Physical properties and optical data**

Popugaevaite is transparent, colourless, with white streak and vitreous lustre. It is non-fluorescent under both ultraviolet rays and an electron beam. Popugaevaite is brittle. Cleavage is perfect on {010}, the fracture is stepped. The Mohs' hardness (determined using a scratch test) is *ca* 3. The density could not be measured because of the paucity of pure material, without inclusions of halite or szaibélyite. The density calculated using the empirical formula and unit-cell volume obtained from single crystal X-ray diffraction data is 1.933 g cm$^{-3}$.

Popugaevaite is optically biaxial (–), α = 1.502(2), β = 1.523(2), γ = 1.530(2) (589 nm). $2V_{\text{meas}}$ = 50(10)º and $2V_{\text{calc}}$ = 59º. Dispersion of optical axes was not observed. In plane polarized light the mineral is colourless and non-pleochroic.

**Infrared spectroscopy**

In order to obtain an infrared (IR) absorption spectrum, popugaevaite powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm$^{-1}$. 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of popugaevaite (Fig. 3) contains bands in the region from 3130 to 3550 cm$^{-1}$ (O–H-stretching vibrations of OH groups and $H_2O$ molecules), at 1646 cm$^{-1}$ (bending vibrations of $H_2O$ molecules), in the range 1290 – 1410 cm$^{-1}$ (mixed modes involving asymmetric stretching vibrations of $BO_3$ triangles and B–O–H bending vibrations), 870 – 1160 cm$^{-1}$ (stretching vibrations of $BO_4$ tetrahedra), in the regions from 690 to 800 cm$^{-1}$ (O–B–O bending vibrations of $BO_3$ triangles) and from 500 to 640 cm$^{-1}$ (mixed O–B–O and B–O–B bending modes combined with librational modes of $H_2O$ molecules). Bands below 500 cm$^{-1}$ are due to lattice modes. The weak band at 2100 cm$^{-1}$ corresponds to a combination mode. The band assignment was made based on IR spectra of orthoborates and compounds containing [B(OH)$_4$]$^-$ anion (Chukanov, 2014; Chukanov and Chervonnyi, 2016).

The IR spectrum of popugaevaite is in general close to that of brianroulstonite (Grice *et al.*, 1997). The main differences are as follows:

(1) In the IR spectrum of brianroulstonite, maximum of the strong absorption in the range of O–H-stretching vibrations is observed at 3363 cm$^{-1}$ and is significantly shifted in comparison with the band of O–H-stretching vibrations with the absorption maximum at 3454 cm$^{-1}$ in the IR spectrum of popugaevaite.

(2) In the IR spectrum of brianroulstonite, additional absorption maximum is observed at 971 cm$^{-1}$ which may correspond to Ca···O–H bending vibrations.

Both these facts confirm the presence of isolated (non-bound with B) $OH^-$ anion in brianroulstonite and the absence of this anion in popugaevaite in which the $OH^-$ group non-bound with B is replaced by $F^-$.

## Chemical composition

The determination of Ca, F and Cl in popugaevaite was carried out using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV and a beam current of 20 nA. The electron beam was rastered to the $5 \times 5$ $\mu m^2$ area. The following standards were used: diopside (Ca), $MgF_2$ (F) and NaCl (Cl). The contents of other elements with atomic numbers > 6, except of oxygen, are below detection limits.

The presence of a significant amount of chlorine in popugaevaite prevents the quantitaive determination of boron by electron microprobe due to the overlap of X-ray emission lines of the $K$ series of B with $L$ lines of Cl. The boron content was determined using ICP-MS. The measurements were carried out with the Element-2 (Thermo Fisher Scientific) instrument which has a high resolution (that avoids interference of components) and sensitivity. Several crystals of the mineral were dissolved in 10 $cm^3$ of 3% $HNO_3$ solution (Merck, Suprapur®) in deionized water (EasyPure). Since the mass of the mineral was too small for accurate weighing, we have determined contents of B and Ca in relative units and further used averaged Ca content, obtained by electron microprobe, for B content calculation. The obtained value is in good agreement with the boron content determined from the crystal structure data (see below).

Special attention was paid to the correctness of fluorine determination in popugaevaite. In particular, we carried out electron microprobe study, under the same conditions, of hilgardite $Ca_2B_5O_9Cl \cdot H_2O$, as a standard of a mineral with stable stoichiometry and the same constituents as in popugaevaite, except of F. This study showed the Ca:Cl ratio very close to 2:1 and the absence (i.e., the content below detection limit) of F.

$H_2O$ was not analysed in popugaevaite because of the paucity of pure material. H ($H_2O$) content was calculated, based on the structure data (see below) and taking into account the charge balance requirement, by stoichiometry: for $(OH)_6(H_2O)_8 = 22$ H atoms per formula unit (*apfu*).

The average (for six spot electron-microprobe analyses for Ca, F and Cl) chemical composition of popugaevaite (wt.%, ranges are in parentheses) is: CaO 28.54 (28.34 – 28.75),

$B_2O_3$ 28.62, F 3.19 (2.97 – 3.31), Cl 11.50 (11.32 – 11.60), $H_2O_{calc}$ 32.83, O=(F,Cl) –3.94, total 100.74.

The analytical total is close to 100 wt.% that demonstrates a good agreement between electron microprobe data for Ca, F, and Cl, ICP-MS data for B and calculated value for H ($H_2O$). The correctness of the obtained chemical data is also confirmed by the excellent value of the Gladstone–Dale compatibility index (Mandarino, 1981): $1 - (K_p/K_c) = -0.026$.

The empirical formula, calculated on the basis of 23 O+F+Cl *apfu* with 22 H *apfu*, is: $Ca_{3.07}B_{4.96}O_{6.03}(OH)_6F_{1.01}Cl_{1.96} \cdot 8H_2O$. The idealized formula is $Ca_3B_5O_6(OH)_6FCl_2 \cdot 8H_2O$ which requires CaO 27.74, $B_2O_3$ 28.70, $H_2O$ 32.70, F 3.13, Cl 11.69, O=(F,Cl) –3.96, total 100 wt%.

Popugaevaite is insoluble in water and slowly dissolves in cold dilute HCl aqueous solution without effervescence. The obtained solution shows characteristic colour reaction with quinalizarin clearly indicating the presence of boron.

**X-ray crystallography and crystal structure determination details**

Single-crystal X-ray diffraction (XRD) studies of popugaevaite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. Data reduction was performed using CrysAlisPro, version 1.171.37.34 (Agilent..., 2014). The data were corrected for Lorentz factor and polarization effects. The crystal structure was solved by direct methods and refined in the space group *Pn* using the SHELX software package (Sheldrick, 2015). Unfortunately, not too high quality of the studied crystal and consequently of the experimental data did not allow good agreement between observed and calculated $F^2$ values: final $R_{hkl}$ = 0.0998 for 4255 reflections with $I>2\sigma(I)$. At the same time, reasonable values of interatomic distances, as well as good agreement between the measured and calculated powder XRD patterns (Table 1) showed that the obtained structure model is correct. Further refinement of the structure was performed by the Rietveld method using this model in order to check whether other possible popugaevaite polytypes exist in the sample and to obtain more precise powder diffraction data.

Powder XRD data of popugaevaite (Table 1) were collected with a Rigaku R-AXIS Rapid II diffractometer equipped with a cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry, Co*K*α radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA and an exposure time of 15 min. The angular resolution of the detector is 0.045° 2Θ (pixel size 0.1 mm). The data were integrated using the software package Osc2Tab (Britvin *et al.*, 2017).

Data treatment and the Rietveld structure analysis were carried out using JANA2006 program package (Petříček *et al.*, 2006). The profiles were modeled using a pseudo-Voigt function. The structure was refined in isotropic approximation of atomic displacements. The $U_{iso}$ values for all

boron atoms were restricted to be equal. In addition, the restriction of equal $U_{iso}$ values was applied to the totality of all O and F atoms. The cation-anion interatomic distances for B-centred tetrahedra and triangles, as well as Ca–F and Cl–O distances, were softly restricted nearby the values obtained for the single-crystal model. Final agreement factors are: $R_{wp}$ = 0.0058, $R_p$ = 0.0043, $R_{obs}$ = 0.0241. The observed and calculated powder XRD diagrams demonstrate a very good compatibility (Fig. 4).

Crystal data, data collection information and structure refinement details for both single-crystal and powder XRD studies of popugaevaite are given in Table 2, coordinates and thermal displacement parameters of atoms in Table 3, selected interatomic distances in Table 4 and bond valence calculations in Table 5.

**Discussion**

Popugaevaite $Ca_3[B_5O_6(OH)_6]FCl_2 \cdot 8H_2O$ is an isostructural analogue of brianroulstonite $Ca_3[B_5O_6(OH)_6](OH)Cl_2 \cdot 8H_2O$ (Grice *et al.*, 1997, 2005) with $F^-$ instead of the $OH^-$ group non-bound with boron[1]. The transformation matrix from the unit cell of brianroulstonite [space group *Pa*, *a* = 17.367 (4), *b* = 8.079 (2), *c* = 8.693 (2) Å, β = 121.56 (2)°, *V* = 1039.3 (6) Å$^3$: Grice *et al.*, 1997] to the conventional unit cell chosen by us for popugaevaite is as follows: 0 0 1 / 0 -1 0 / 1 0 1. This results in the unit-cell parameters of brianroulstonite *a* = 8.693, *b* = 8.079, *c* = 14.8036 Å and β = 91.536° close to those of popugaevaite (Table 6).

The crystal structure of popugaevaite (Fig. 5), as well as that of brianroulstonite, is based upon the layers of twelve-membered rings of alternating B-centred polyhedra: $BO_3$ triangles and $BO_2(OH)_2$ tetrahedra (Fig. 6). Each ring consists of six triangles and six tetrahedra and shares three borate polyhedra with adjacent rings. Within the rings of the borate sheets three crystallographically non-equivalent Ca sites are located. All Ca cations have eight-fold coordination $CaO_2F(OH)_3(H_2O)_2$ for Ca1 and Ca3 and $CaO_2F(OH)_2(H_2O)_3$ for Ca2. Ca-centred polyhedra share F-(OH) edges to form triads with common F vertex. All $H_2O$ molecules participate in Ca coordination except Ow4 which is only hydrogen-bonded within the structure. The Cl atoms are located between the calcium-borate slabs and cross-link them through the complicate system of H bonds in which Cl atoms play the role of the only acceptors of H-bonds with the OH–Cl distances in the range from 3.15 to 3.25 for Cl1 and 3.14 – 3.26 Å for Cl2 (Table 4).

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[1] No data on fluorine was reported for brianroulstonite (Grice *et al.*, 1997, 2005). For confirmation of the F absence in brianroulstonite, we had specially contacted with Dr. Joel Grice and asked him to specify this point. Dr. Grice answered that the suggestion of the possible fluorine presence in brianroulstonite was checked during the first study and F content turned out below detection limit.

The fundamental building block (FBB) in the structures of brianroulstonite and popugaevaite, according to the classification of FBB in borates (Burns *et al.*, 1995; Grice *et al.*, 1999), can be presented as 6Δ6□:<Δ□Δ□Δ□Δ□Δ□Δ□>. Among minerals, twelve-membered borate rings were reported also in pringleite and ruitenbergite, two polymorphs of $Ca_9[B_{26}O_{34}(OH)_{24}]Cl_4 \cdot 13H_2O$ (Grice *et al.*, 1994), and in penobsquisite, $Ca_2Fe[B_9O_{13}(OH)_6]Cl \cdot 4H_2O$ (Grice *et al.*, 1996), where the sheets of dodecaborate rings are linked to form frameworks. Isolated twelve-membered rings with alternating boron tetrahedra and triangles were reported for satimolite, $KNa_2(Al_5Mg_2)[B_{12}O_{18}(OH)_{12}](OH)_6Cl_4 \cdot 4H_2O$ (Pekov *et al.*, 2018).

The borate layers $[B_5O_6(OH)_6]$ formed by twelve-membered rings in popugaevaite are topologically close to the silicate tetrahedral nets in zeophyllite $Ca_{13}(F,OH)_{10}[Si_5O_{14}]_2 \cdot 6H_2O$ and britvinite $[Pb_7(OH)_3F(BO_3)_2(CO_3)][Mg_{4.5}(OH)_3(Si_5O_{14})]$ (Yakubovich *et al.*, 2008). The main difference is that in popugaevaite both triangles and tetrahedra participate in the fundamental building blocks whereas in both aforementioned silicates the layers are formed exceptionally by tetrahedra. As a result, borate and silicate layers are characterized by different formulae: $[B_5O_6(OH)_6]$ *vs* $[Si_5O_{14}]$.

## Acknowledgements

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Table 1. Powder X-ray diffraction data (*d* in Å) of popugaevaite.

| $I_{obs}$ | $d_{obs}$ | $I_{calc}$* | $d_{calc}$ | h k l |
|---|---|---|---|---|
| **100** | **8.12** | 100 | 8.103 | 010 |
| 7 | 7.43 | 4 | 7.426 | 101 |
| **12** | **7.13** | 12 | 7.108 | 011 |
| 3 | 5.946 | 3 | 5.930 | 110 |
| 4 | 5.484 | 2, 2 | 5.475, 5.466 | 111, 012 |
| 2 | 4.668 | 2 | 4.666 | -112 |
| 4 | 4.603 | 4 | 4.592 | 112 |
| 8 | 4.353 | 4, 4 | 4.352, 4.338 | 200, -103 |
| 2 | 4.225 | 2 | 4.215 | 013 |
| **27** | **4.058** | 27 | 4.051 | 020 |
| 2 | 3.913 | 2 | 3.908 | 021 |
| 5 | 2.834 | 2, 3 | 2.834, 2.824 | 210, -113 |
| 4 | 3.768 | 3 | 3.764 | 113 |
| 6 | 3.715 | 3 | 3.713 | 202 |
| **15** | **3.577** | 15, 1, 2 | 3.573, 3.556, 3.554 | -121, 121, 022 |
| 4 | 3.438 | 4 | 3.434 | -212 |
| 6 | 3.376 | 5, 3 | 3.375, 3.367 | 212, 014 |
| 2 | 3.168 | 2 | 3.163 | -114 |
| 1 | 3.128 | 0.5, 0.5 | 3.132, 3.118 | 023, 114 |
| **10** | **2.936** | 11 | 2.932 | 123 |
| **16** | **2.834** | 10, 10 | 2.834, 2.824 | 301, -105 |
| 2 | 2.787 | 1, 2 | 2.787, 2.783 | 204, 105 |
| 5 | 2.739 | 3, 3 | 2.737, 2.733 | 222, 024 |
| 6 | 2.697 | 2, 3, 2 | 2.701, 2.697, 2.691 | 030, -311, -214 |
| 6 | 2.664 | 3, 5 | 2.667, 2.657 | -115, 031 |
| 3 | 2.636 | 2, 1 | 2.635, 2.632 | 214, 115 |
| 8 | 2.541 | 1, 1, 4, 3 | 2.544, 2.544, 2.538, 2.537 | -131, 312, 131, 032 |
| 3 | 2.476 | 1, 1 | 2.475, 2.468 | 303, 006 |
| 5 | 2.415 | 4 | 2.413 | -313 |
| 3 | 2.369 | 1, 0.5, 0.5 | 2.369, 2.368, 2.367 | 033, -215, 313 |
| 6 | 2.323 | 3, 0.5, 3 | 2.322, 2.320, 2.317 | 321, 215, -125 |
| 5 | 2.298 | 2, 1, 0.5, 1 | 2.297, 2.295, 2.294, 2.293 | 224, 230, 125, -133 |
| **10** | **2.283** | 11 | 2.280 | 133 |
| 3 | 2.201 | 4 | 2.200 | -232 |
| 4 | 2.179 | 1, 2, 3 | 2.184, 2.182, 2.176 | 232, 034, 400 |
| 1 | 2.146 | 2 | 2.144 | -323 |
| 2 | 2.127 | 3 | 2.125 | 206 |
| 9 | 2.104 | 4, 4, 1 | 2.108, 2.101, 2.101 | 026, 410, -402 |



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| 4 | 2.050 | 3, 2 | 2.056, 2.048 | 216, 305 |
|---|---|---|---|---|
| 3 | 2.030 | 1, 3 | 2.031, 2.026 | -315, 040 |
| 2 | 2.008 | 2 | 2.007 | 041 |
| 2 | 1.976 | 1, 1 | 1.977, 1.973 | 330, 140 |
| 1 | 1.958 | 1, 0.5 | 1.962, 1.955 | -234, 331 |
| 3 | 1.897 | 3 | 1.896 | -404 |
| 2 | 1.883 | 3 | 1.882 | 226 |
| 3 | 1.865 | 2, 2 | 1.865, 1.863 | -422, -325 |
| 2 | 1.850 | 1, 2 | 1.851, 1.846 | 008, 422 |
| 3 | 1.839 | 1, 1, 0.5, 1 | 1.841, 1.836, 1.836, 1.835 | -127, 240, 217, -143 |
| 3 | 1.826 | 0.5, 2 | 1.825, 1.825 | -235, 333 |
| 1 | 1.809 | 1 | 1.810 | 414 |
| 3 | 1.692 | 2, 1, 1 | 1.695, 1.694, 1.691 | -511, 430, -317 |
| 2 | 1.656 | 1, 1, 1 | 1.658, 1.657, 1.653 | -432, -335, 218 |
| 3 | 1.650 | 1, 2 | 1.652, 1.648 | -244, 341 |
| 1 | 1.459 | 0.5, 1 | 1.459, 1.456 | -531, -337 |
| 1 | 1.410 | 1 | 1.409 | -254 |
| 1 | 1.386 | 1 | 1.384 | -444 |

*For the calculated pattern, only reflections with intensities ≥0.5 are given. The strongest reflections are marked in boldtype. The powder pattern was calculated using Diamond, Version 3.2k.

Table 2. Crystal data, data collection information and structure refinement details for popugaevaite.

| | Rietveld refinement | Single-crystal data |
|---|---|---|
| Formula | $Ca_3[B_5O_6(OH)_6]FCl_2 \cdot 8H_2O$ | |
| Formula weight | 584.2 | |
| Temperature, K | 293(2) | |
| Radiation and wavelength, Å | $CoK\alpha$; 1.79021 | $MoK\alpha$; 0.71073 |
| Crystal system, space group, $Z$ | Monoclinic, $Pn$, 2 | |
| Unit cell dimensions, Å/° | $a = 8.7055(11)$ $b = 8.1025(11)$ $\beta = 91.367(7)$ $c = 14.812(2)$ | $a = 8.6936(3)$ $b = 8.0933(3)$ $\beta = 91.460(3)$ $c = 14.8219(5)$ |
| $V$, Å$^3$ | 1044.5(2) | 1042.53(6) |
| Absorption coefficient $\mu$, mm$^{-1}$ | 15.373 | 1.143 |
| F$_{000}$ | 576 | |
| Diffractometer | Rigaku R-Axis II (cylindrical image plate detector, $d$ = 127.4 mm) | Xcalibur S CCD |
| Range for data collection, ° | 2θ from 10.00 to 140.00 | θ from 2.687 to 27.091 $-11 \leq h \leq 11$, $-10 \leq k \leq 10$, $-18 \leq l \leq 18$ |
| Final $R$ indices | $R_{exp} = 0.0081$, $R_{wp} = 0.0058$, $R_p = 0.0043$, $R_{obs} = 0.0241$ | $R1 = 0.0998$, |

| | | |
|---|---|---|
| | | $wR2 = 0.2663$ [$I>2\sigma(I)$] |
| | | $R1 = 0.1040$, |
| | | $wR2 = 0.2726$ (all data) |
| GoF | 0.72 | 1.163 |
| Largest diff. peak and hole | 0.22 and -0.21 e/Å$^3$ | 1.82 and -1.26 e/Å$^3$ |
| Other data | | Crystal size $0.08 \times 0.18 \times 0.20$ mm$^3$ |
| | | Structure solution – direct methods |
| | | Refinement method – full-matrix least-squares on $F^2$ |
| | | Absorption correction: multi-scan |

Table 3. Coordinates and isotropic displacement parameters ($U_{\text{iso}}$, in Å$^2$) of atoms for popugaevaite (after Rietveld refinement)

| Site | $x$ | $y$ | $z$ | $U_{\text{iso}}$ |
|---|---|---|---|---|
| Ca1 | 0.843(2) | 0.970(2) | 0.0896(12) | 0.031(8) |
| Ca2 | 0.337(2) | 0.7896(16) | 0.8223(10) | 0.027(6) |
| Ca3 | 0.4777(16) | 1.000(3) | 0.2096(10) | 0.017(7) |
| B1 | 0.635(4) | 1.000(5) | 0.691(3) | 0.027(11) |
| B2 | 0.697(5) | 0.024(13) | 0.531(3) | 0.027(11) |
| B3 | 0.966(5) | 0.980(4) | 0.475(3) | 0.027(11) |
| B4 | 0.483(6) | 0.018(6) | 0.405(3) | 0.027(11) |
| B5 | 0.196(5) | 0.019(11) | 0.360(3) | 0.027(11) |
| Cl1 | 0.1341(18) | 0.489(3) | 0.1140(11) | 0.047(10) |
| Cl2 | 0.895(2) | 0.502(2) | 0.8873(11) | 0.039(9) |
| O1 | 0.550(5) | 0.038(6) | 0.499(3) | 0.006(3) |
| O2 | 0.052(5) | 0.043(6) | 0.397(3) | 0.006(3) |
| O3 | 0.816(6) | 0.941(5) | 0.916(3) | 0.006(3) |
| O4 | 0.988(6) | 0.795(4) | 0.484(2) | 0.006(3) |
| O5 | 0.547(6) | 0.939(4) | 0.050(3) | 0.006(3) |
| O6 | 0.305(4) | 0.960(6) | 0.966(3) | 0.006(3) |
| O7 | 0.737(5) | 0.977(6) | 0.773(3) | 0.006(3) |
| O8 | 0.553(5) | 0.147(4) | 0.351(3) | 0.006(3) |
| O9 | 0.508(5) | 0.873(3) | 0.345(3) | 0.006(3) |
| O10 | 0.252(4) | 0.986(6) | 0.119(3) | 0.006(3) |
| O11 | 0.014(5) | 0.127(4) | 0.175(3) | 0.006(3) |
| O12 | 0.544(5) | 0.155(4) | 0.695(3) | 0.006(3) |
| F | 0.2322(19) | 0.975(3) | 0.7202(12) | 0.006(3) |
| Ow1 | 0.433(3) | 0.676(5) | 0.1928(14) | 0.016(5) |
| Ow2 | 0.779(5) | 0.265(5) | 0.045(2) | 0.016(5) |
| Ow3 | 0.286(3) | 0.316(5) | 0.5697(16) | 0.016(5) |
| Ow4 | 0.801(5) | 0.721(4) | 0.318(3) | 0.016(5) |

| | | | |
|---|---|---|---|
| Ow5 | 0.458(3) | 0.319(6) | 0.171(3) | 0.016(5) |
| Ow6 | 0.244(6) | 0.559(4) | 0.725(3) | 0.016(5) |
| Ow7 | 0.057(3) | 0.429(4) | 0.3180(14) | 0.016(5) |
| Ow8 | 0.301(4) | 0.589(5) | 0.930(2) | 0.016(5) |

Table 4. Selected interatomic distances (Å) in the structure of popugaevaite (after Rietveld refinement).

| | | | | |
|---|---|---|---|---|
| Ca1–F | 2.22(2) | | B1–O11 | 1.49(5) |
| –O1 | 2.28(5) | | –O12 | 1.49(5) |
| –O11 | 2.31(4) | | –O7 | 1.50(6) |
| –Ow3 | 2.39(4) | | –O10 | 1.50(6) |
| –O12 | 2.53(4) | | <B1–O> | 1.495 |
| –Ow2 | 2.54(4) | | | |
| –O3 | 2.59(5) | | B2–O1 | 1.36(6) |
| –O5 | 2.64(5) | | –O6 | 1.37(6) |
| <Ca1–φ> | 2.44 | | –O10 | 1.38(6) |
| | | | <B2–O> | 1.37 |
| Ca2–F | 2.30(3) | | | |
| –Ow8 | 2.31(4) | | B3–O2 | 1.48(6) |
| –Ow6 | 2.48(4) | | –O4 | 1.52(5) |
| –O2 | 2.54(5) | | –O5 | 1.46(6) |
| –O6 | 2.56(5) | | –O6 | 1.49(6) |
| –O8 | 2.57(5) | | <B3–O> | 1.49 |
| –Ow7 | 2.61(3) | | | |
| –O11 | 2.78(5) | | B4–O1 | 1.51(6) |
| <Ca2–φ> | 2.52 | | –O3 | 1.50(7) |
| | | | –O8 | 1.46(6) |
| Ca3–F | 2.22(2) | | –O9 | 1.49(6) |
| –O9 | 2.26(4) | | <B4–O> | 1.49 |
| –O7 | 2.32(5) | | | |
| –O10 | 2.36(4) | | B5–O2 | 1.39(6) |
| –O8 | 2.48(5) | | –O3 | 1.36(7) |
| –O5 | 2.51(5) | | –O7 | 1.35(6) |
| –Ow5 | 2.65(5) | | <B5–O> | 1.37 |
| –Ow1 | 2.67(5) | | | |
| <Ca3–φ> | 2.43 | | | |
| | | | | |
| Cl1–O11=OH | 3.25(4) | | Cl2–O8=OH | 3.21(4) |
| Cl1–O12=OH | 3.23(4) | | Cl2–O9=OH | 3.26(3) |
| Cl1–Ow1 | 3.21(3) | | Cl2–Ow1 | 3.24(3) |
| Cl1–Ow5 | 3.23(4) | | Cl2–Ow2 | 3.21(4) |
| Cl1–Ow7 | 3.15(2) | | Cl2–Ow3 | 3.25(4) |
| Cl1–Ow8 | 3.22(4) | | Cl2–Ow7 | 3.14(3) |

Table 5. Bond valence calculations for popugaevaite.

| Site | Ca1 | Ca2 | Ca3 | B1 | B2 | B3 | B4 | B5 | Σ |
|---|---|---|---|---|---|---|---|---|---|
| O1 | 0.40 | | | | 1.03 | | 0.68 | | 2.11 |
| O2 | | 0.21 | | | | 0.74 | | 0.95 | 1.90 |
| O3 | 0.19 | | | | | | 0.70 | 1.03 | 1.92 |
| O4 = OH | | | | | | 0.66 | | | 0.66 |
| O5 = OH | 0.17 | | 0.23 | | | 0.78 | | | 1.18 |
| O6 | | 0.20 | | | 1.01 | 0.72 | | | 1.93 |
| O7 | | | 0.36 | 0.70 | | | | 1.06 | 2.12 |
| O8 = OH | | 0.20 | 0.25 | | | | 0.78 | | 1.23 |
| O9 = OH | | | 0.42 | | | | 0.72 | | 1.14 |
| O10 | | | 0.33 | 0.70 | 0.98 | | | | 2.01 |
| O11 = OH | 0.37 | 0.12 | | | 0.72 | | | | 1.21 |
| O12 = OH | 0.22 | | | | 0.72 | | | | 0.94 |
| F | 0.36 | 0.29 | 0.36 | | | | | | 1.01 |
| Ow1 = H$_2$O | | | 0.15 | | | | | | 0.15 |
| Ow2 = H$_2$O | 0.21 | | | | | | | | 0.21 |
| Ow3 = H$_2$O | 0.31 | | | | | | | | 0.31 |
| Ow4 = H$_2$O | | | | | | | | | 0.00 |
| Ow5 = H$_2$O | | | 0.16 | | | | | | 0.16 |
| Ow6 = H$_2$O | | 0.25 | | | | | | | 0.25 |
| Ow7 = H$_2$O | | 0.18 | | | | | | | 0.18 |
| Ow8 = H$_2$O | | 0.37 | | | | | | | 0.37 |
| Σ | 2.23 | 1.82 | 2.26 | 2.84 | 3.02 | 2.90 | 2.88 | 3.04 | |

Bond-valence parameters for B-O, Ca-O are taken from Gagné & Hawthorne (2015) and for Ca-F from Brese & O'Keeffe (1991).



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Table 6. Comparative data for popugaevaite and brianroulstonite.

| Mineral | Popugaevaite | Brianroulstonite |
|---|---|---|
| Formula | $Ca_3[B_5O_6(OH)_6]FCl_2 \cdot 8H_2O$ | $Ca_3[B_5O_6(OH)_6](OH)Cl_2 \cdot 8H_2O$ |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *Pn* | *Pn** |
| *Unit cell data*: | | |
| *a*, Å | 8.7055(11) | 8.693 |
| *b*, Å | 8.1025(11) | 8.079 |
| *c*, Å | 14.812(2) | 14.8036 |
| β, º | 91.367(7) | 91.536 |
| *V*, Å$^3$ | 1044.5(2) | 1039 |
| *Z* | 2 | 2 |
| Strongest | 8.12 – 100 | 8.10 – 100 |
| reflections of | 7.13 – 12 | 4.04 – 40 |
| the powder | 4.058 – 27 | 2.535 – 20 |
| XRD pattern: | 3.577 – 15 | 2.276 – 20 |
| *d*, Å – *I* | 2.936 – 10 | |
| | 2.834 – 16 | |
| | 2.283 – 10 | |
| *Optical data*: | | |
| α | 1.502(2) | 1.506(2) |
| β | 1.523(2) | 1.527(2) |
| γ | 1.530(2) | 1.532(2) |
| optical sign, 2*V* | –50º | –56º |
| Sources | This work | Grice *et al*., 1997 |

*Brianroulstonite was originally described with space group *Pa* and the following unit-cell parameters: *a* = 17.367(4), *b* = 8.079(2), *c* = 8.693(2) Å, β = 121.56(2)° and *V* = 1039.3(6) Å$^3$ (Grice *et al*., 1997); the transformation matrix from this unit cell to the conventional unit cell chosen by us for popugaevaite is as follows: 0 0 1 / 0 -1 0 / 1 0 1 (see text).
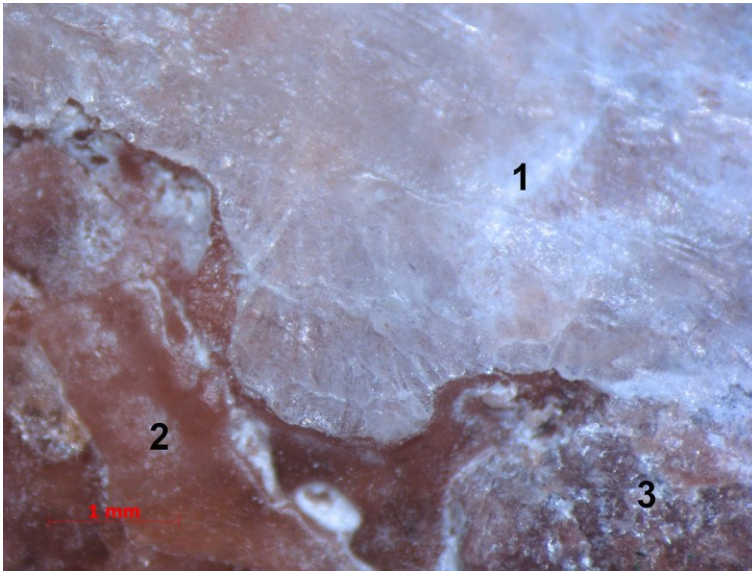
**Figure 1**. Colourless crust of popugaevaite (1) with halite (2) on ekaterinite (3). FOV width: 9.5 mm.
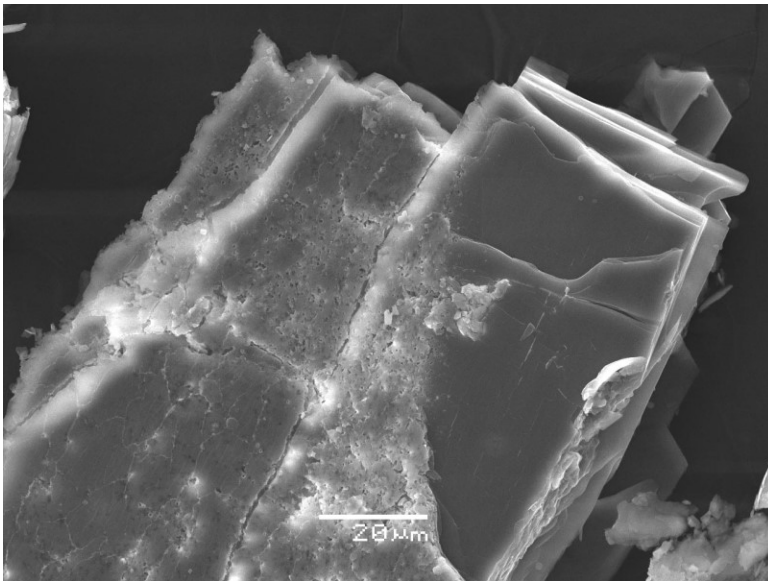


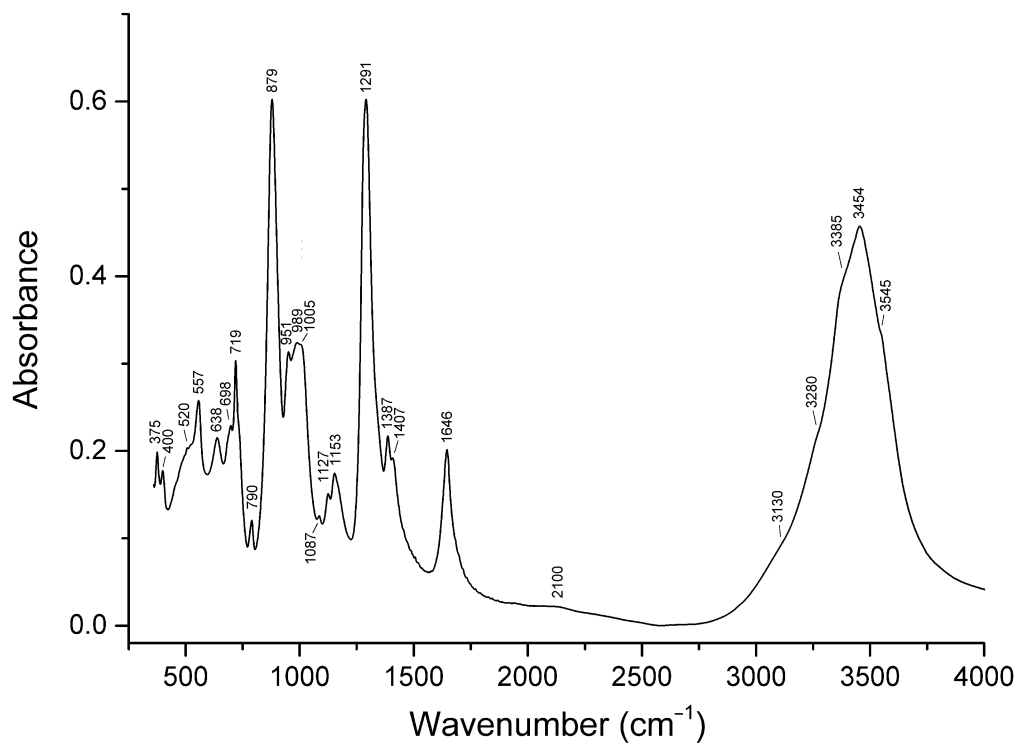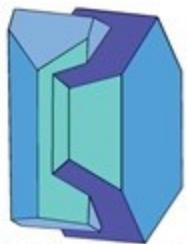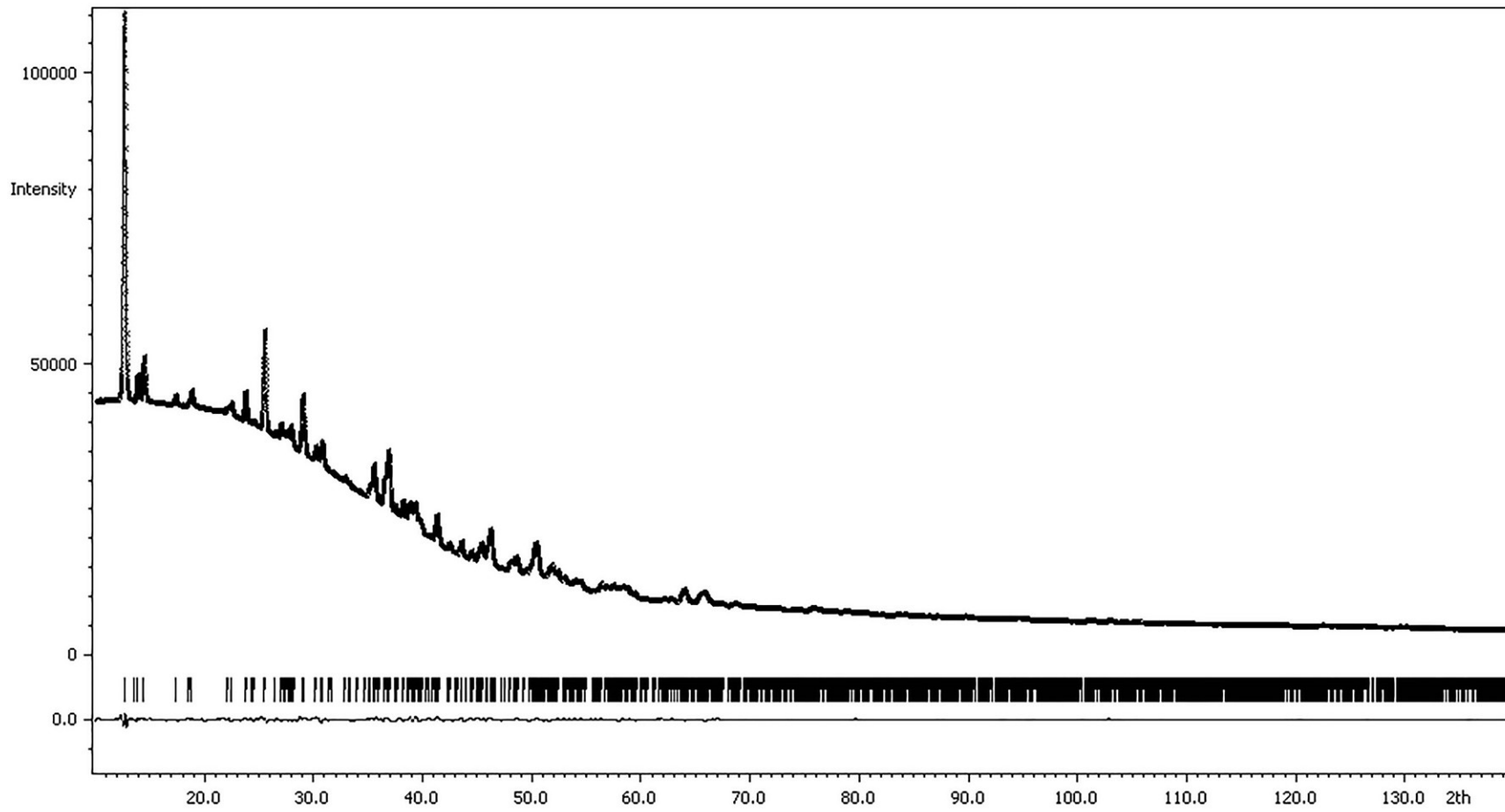**Figure 2**. Coarse crystal of popugaevaite. SEM (SE) image.

**Figure 3**. Infrared apsorption spectrum of popugaevaite.

**Figure 4**. Observed and calculated powder X-ray diffraction patterns of popugaevaite. The solid line corresponds to calculated data, the crosses correspond to the observed pattern, vertical bars mark all possible Bragg reflections. The difference between the observed and calculated patterns is shown by curve at the bottom.
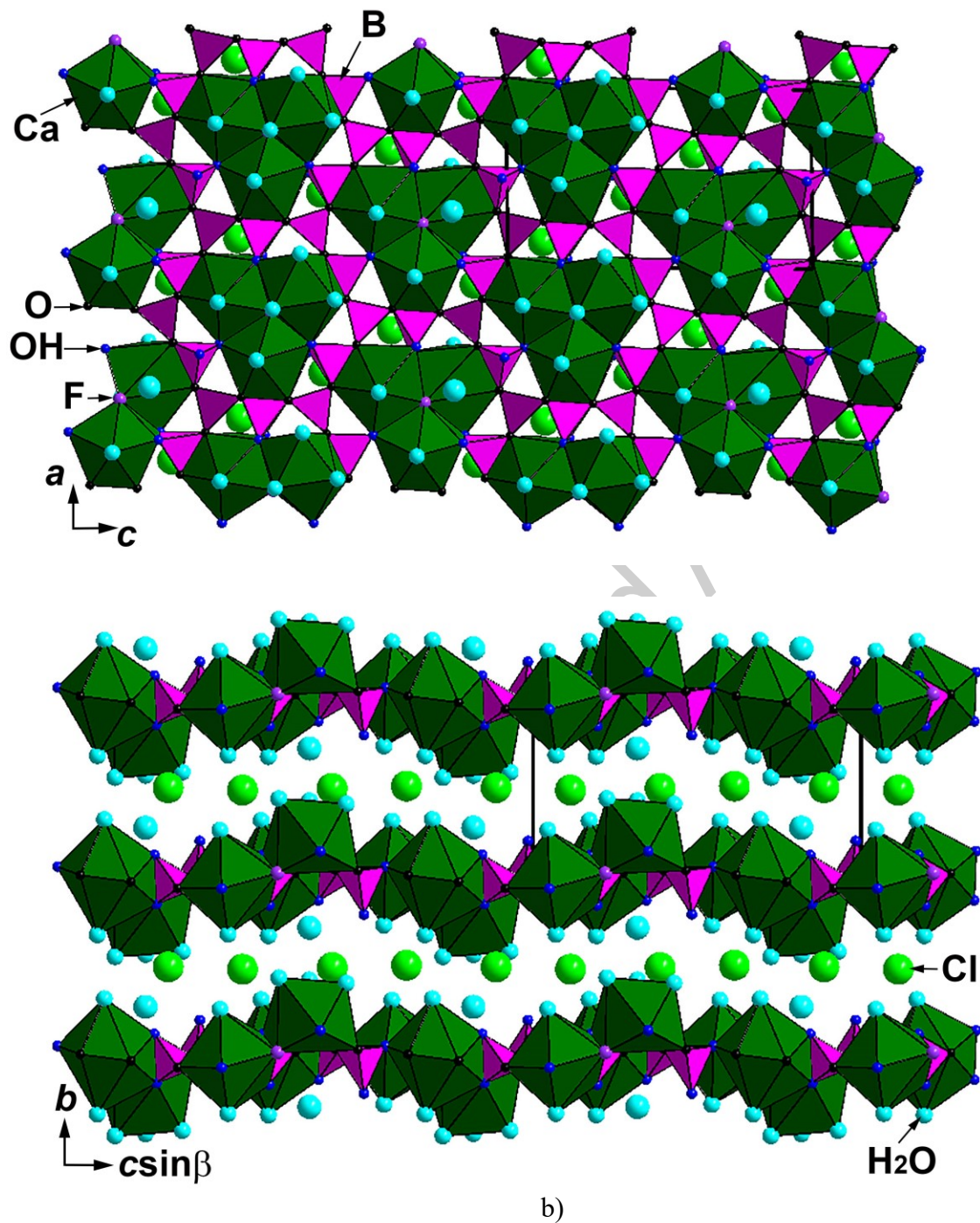
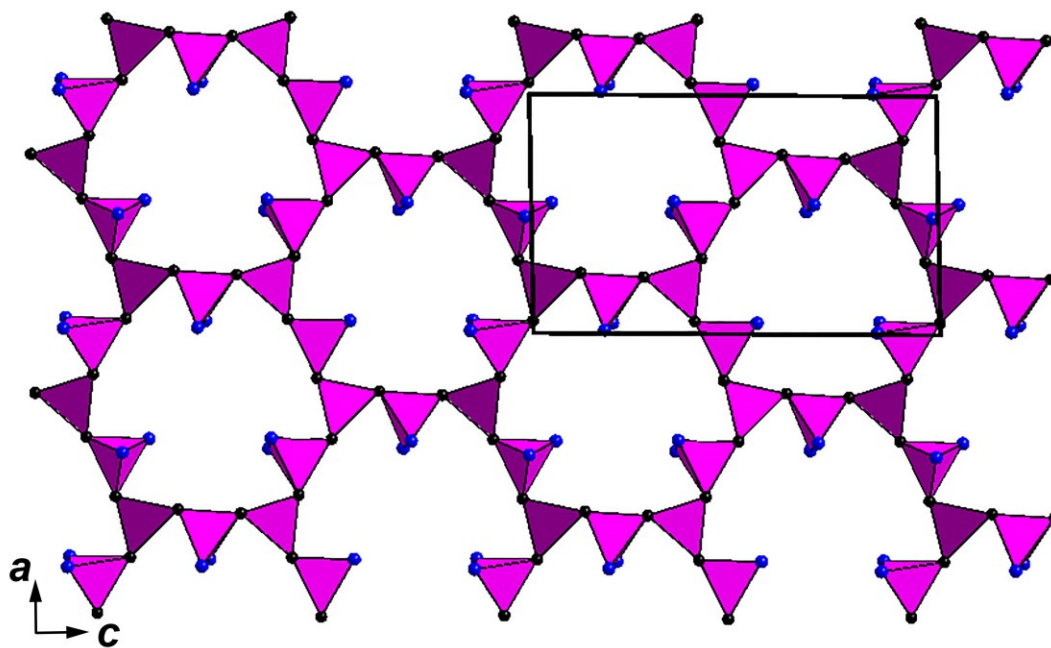**Figure 5**. The crystal structure of popugaevaite projected along the *b* (a) and *a* (b) axes. The unit cell is outlined.

**Figure 6**. Borate layer in the structure of popugaevaite. The unit cell is outlined.