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Article

Yarzhemskiite, $K[B_5O_7(OH)_2]\cdot H_2O$, a new mineral from the Chelkar salt dome, Western Kazakhstan

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Abstract

The new mineral yarzhemskiite, $K[B_5O_7(OH)_2]\cdot H_2O$, was found in a halite–sylvite evaporite rock at the Chelkar salt dome, Western Kazakhstan Region, Kazakhstan. It is also associated with carnallite, polyhalite, gypsum, strontioginorite, satimolite and quartz. Yarzhemskiite occurs as separate thick tabular, short prismatic or equant crystals up to 0.5 mm × 0.7 mm × 1 mm and grains having irregular outlines up to 1 mm × 1.5 mm × 2 mm. The mineral is transparent, colourless, with vitreous lustre. It is brittle, the Mohs' hardness is *ca* 2½. Cleavage is perfect on {100}. D_{meas} is 2.13(1) and D_{calc} is 2.112 g cm^{-3}. Yarzhemskiite is optically biaxial (+), α = 1.484(2), β = 1.508(2), γ = 1.546(2), $2V_{meas}$ = 75(10)° and $2V_{calc}$ = 80°. Chemical composition (wt.%, electron microprobe, H_2O was calculated by stoichiometry) is: Na_2O 0.01, K_2O 17.84, CaO 0.07, B_2O_3 67.21, H_2O_{calc} 13.91, total 99.04. The empirical formula based on 10 O atoms per formula unit is $K_{0.98}B_{5.005}O_7(OH)_2\cdot H_2O$. Yarzhemskiite is monoclinic, $P2_1/c$, a = 9.47340(18), b = 7.52030(16), c = 11.4205(2) Å, β = 97.3002(17)°, V = 807.03(3) Å^3 and Z = 4. The strongest reflections of the powder XRD pattern [d,Å(I,%)(hkl)] are: 9.39(86)(100), 4.696 (41)(200), 3.296(18)($\bar{1}$13), 3.130(19)(022, 300), 2.935(42)(220), 2.898(100)($\bar{3}$02, $\bar{2}$21, 310), 2.832(56)(004) and 1.867(18)($\bar{2}$25). The crystal structure was solved based on single-crystal X-ray diffraction data, R_1 = 3.36%. The structure contains infinite chains built by boron-centred polyhedra. The basic structural unit of the chain is a double ring $B_5O_7(OH)_2$ consisting of one BO_4 tetrahedron and four BO_3 triangles. K^+ cations centre ten-fold polyhedra which form, together with the borate chains $[B_5O_7(OH)_2]^-_\infty$, layers linked with each other only *via* H bonds. The mineral is named in honour of the Russian geologist, petrologist and mineralogist Yakov Yakovlevich Yarzhemskii (1901–?), a specialist in petrology of evaporite rocks and mineralogy and genesis of boron deposits related to evaporites.

Keywords: yarzhemskiite, new mineral, hydrous potassium borate, larderellite, crystal structure, evaporite deposit, Chelkar salt dome, Western Kazakhstan

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Introduction

The Chelkar salt dome in the North Caspian Region, Western Kazakhstan is one of the classic localities of diverse borate mineralisation formed in evaporites. Chelkar was actively studied, including prospecting for boron, between the 1950s and 1970s based on drillcores of numerous boreholes. A geological description of the Chelkar salt dome was given by Oshakpaev (1974) and data on mineralogy and genesis of Chelkar borates obtained in this period have been summarised by Yarzhemskii (1968, 1984) and Avrova *et al.* (1968).

Chelkar is the type locality of several boron minerals discovered more than fifty years ago, namely aksaite (Blazko *et al.*, 1962), halurgite (Lobanova, 1962), metaborite (Lobanova and Avrova, 1964) and insufficiently studied borates strontioborite (Lobanova, 1960) and chelkarite (Avrova *et al.*, 1968). More recent data on borate minerals from Chelkar were reported by Malinko *et al.* (1991), Korotchenkova and Chaikovskiy (2016) and Pekov *et al.* (2018*b*, 2019).

The new mineral described in the present paper was found during the studies of core from a borehole recently drilled at the Chelkar salt dome for prospecting of potassium salts. Initially this borate was misidentified as 'santite', based on the electron-microprobe data (Korotchenkova and Chaikovskiy, 2016). Later, X-ray diffraction studies showed that it is a representative of the larderellite structure type. The new mineral, a potassium analogue of larderellite has been named yarzhemskiite (Cyrillic: яржемскиит) in honour of the Russian geologist, petrologist and mineralogist Yakov Yakovlevich Yarzhemskii

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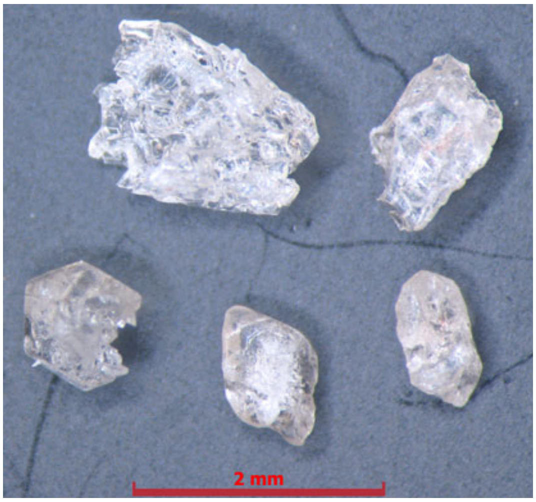

Fig. 1. The largest found crystals (lower row) and grains with irregular outlines of yarzhemskiite. Field of view, width: 4.2 mm. Photo: I.V. Pekov and A.V. Kasatkin.

(1901–?), a specialist in petrology of evaporite rocks and mineralogy and genesis of boron deposits related to evaporites. Prof. Yarzhemskii worked in the All-Union Research Institute of Halurgy (Leningrad) and made a great contribution to studies of boron-bearing sedimentary rocks and boron deposits of Western Kazakhstan, including Chelkar (see, e.g. Yarzhemskii, 1968, 1984).

Both new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification, (IMA2018-019, Pekov *et al.*, 2018*a*). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 96257.

Occurrence and general appearance

The new mineral was found in core of borehole #800 (depth 344–347 m) drilled at the Chelkar salt dome, near Chelkar (Shalkar) lake, Western Kazakhstan Region, Kazakhstan.

Yarzhemskiite occurs as separate crystals or grains having irregular outlines embedded in a halite–sylvite rock (sylvinite). Other associated minerals are carnallite, polyhalite, gypsum, strontioginorite, satimolite and quartz. Yarzhemskiite was formed as a result of diagenesis or of the post-diagenesis processes, probably related to salt diapirism, in boron-bearing evaporite rocks. It is likely that the formation of yarzhemskiite and associated borates accompanies the recrystallisation of sylvinite.

Crystals of the new mineral are thick tabular (flattened on [010], with the {010} pinacoid as the major crystal form), slightly elongate (short prismatic) or equant, commonly coarse, with a sculptured and/or cavernous surface. Well-formed crystals, resembling typical gypsum crystals in morphology, are up to 0.5 mm × 0.7 mm × 1 mm (typically much less) whereas grains having irregular outlines are up to 1 mm × 1.5 mm × 2 mm. Crystals and grains of yarzhemskiite, separated after dissolution of host sylvinite in water, are shown in Figs 1 and 2. Yarzhemskiite crystals typically contain inclusions of halite, sylvite and quartz.

Physical properties and optical data

Yarzhemskiite is transparent, colourless, with white streak and vitreous lustre. The mineral is non-fluorescent under both

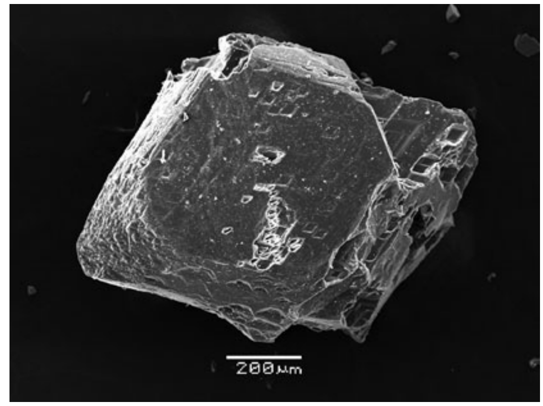

Fig. 2. Yarzhemskiite crystal. Scanning electron microscopy (secondary electron) image.

ultraviolet rays and an electron beam. Yarzhemskiite is brittle. Cleavage is perfect on {100}, the fracture is stepped. The Mohs' hardness is *ca* 2½. The density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.13(1) g cm^{-3}. The density calculated using the empirical formula is 2.112 g cm^{-3}.

Yarzhemskiite is optically biaxial (+), $\alpha = 1.484(2)$, $\beta = 1.508(2)$, $\gamma = 1.546(2)$ (589 nm). $2V_{meas} = 75(10)°$ and $2V_{calc} = 80°$. Dispersion of optical axes was not observed. Orientation: $Y = b$ and $Z \wedge c = 6(1)°$. In plane polarised light the mineral is colourless and non-pleochroic.

Infrared spectroscopy

The infrared (IR) absorption spectrum of yarzhemskiite was obtained for a powdered sample mixed with anhydrous KBr and pelletised. The pellet was analysed in the Institute of Problems of Chemical Physics of the Russian Academy of Sciences (Chernogolovka, Russia) using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm^{-1}. The sampling scan number was 16. The IR spectrum of a pure KBr disc was used as a reference.

The IR spectrum of yarzhemskiite (Fig. 3) contains bands of O–H-stretching vibrations corresponding to medium strength (at 3435 cm^{-1}, with the shoulders at 3400 and 3275 cm^{-1}) and strong (at 2920 cm^{-1}) hydrogen bonds. According to the correlation between O–H stretching frequencies in IR spectra of minerals and O···O distances (from structural data) established by Libowitzky (1999), these wavenumbers correspond to the O···O distances between O atoms of donor and acceptor groups of 2.82, 2.80, 2.73 and 2.63 Å, respectively. These values are in agreement with the *D*···*A* distances of ~2.82, 2.79, 2.68 and 2.62 Å obtained from structural data (see below).

The band at 1624 cm^{-1} is due to H–O–H bending vibrations of H_2O molecules. The bands in the ranges 1200–1500 and 1000–1100 cm^{-1} correspond to B–O-stretching vibrations of BO_3 and BO_4 polyhedra, respectively. The band at 938 cm^{-1} with the shoulder at 950 cm^{-1} is assigned to B–O–H bending vibrations (the splitting is due to resonance between two neighbouring BOH groups). The bands in the range 600–800 cm^{-1} are mainly due to O–B–O bending vibrations. The bands below 600 cm^{-1} correspond to lattice modes involving vibrations of large structural fragments and librational vibrations of H_2O molecules. Weak bands

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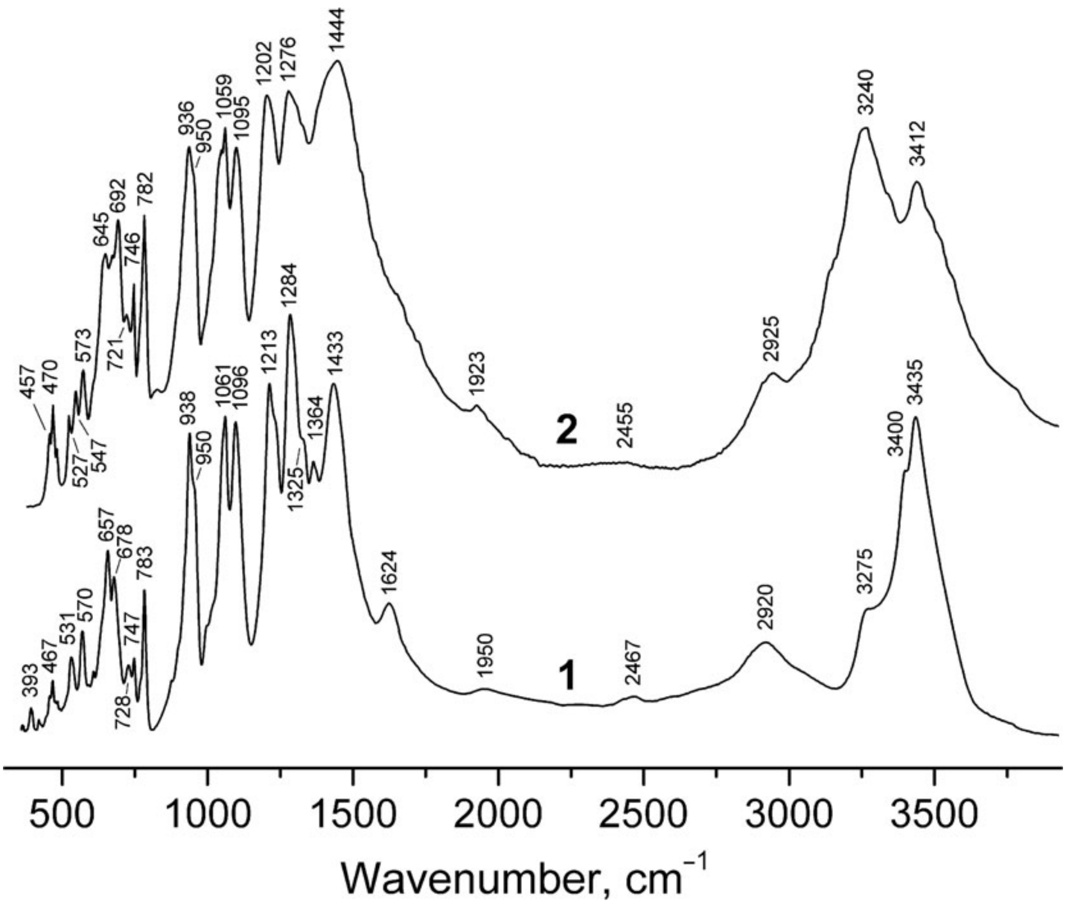

Fig. 3. Powder IR absorption spectra of (1) yarzhemskiite and (2) larderellite from its type locality, Larderello, Pisa Province, Tuscany, Italy (spectrum B91 in: Chukanov, 2014).

in the range 1900–2500 cm^{-1} are overtones and combination modes.

The IR spectrum of larderellite (Fig. 3) is similar to that of yarzhemskiite, but contains additional strong bands at 3240 cm^{-1} (stretching vibrations of NH_4^+ cations), 1444 cm^{-1} (taking into account a high width, this band is to be assigned to a superposition of mixed modes involving B–O-stretching vibrations of BO_3 polyhedra and bending vibrations of NH_4^+ cations), as well as the distinct band at 692 cm^{-1} tentatively assigned to librational vibrations of NH_4^+ cations. Based on these features, larderellite and yarzhemskiite can be easily distinguished.

Chemical composition

Chemical data for yarzhemskiite were obtained 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, Department 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 µm × 5 µm area. The following standards were used: albite (Na), microcline (K), diopside (Ca) and BN (B). Contents of other elements with atomic numbers higher than carbon are below their detection limits.

The average (for five spot analyses) chemical composition of yarzhemskiite (wt.%, ranges are in parentheses) is: Na_2O 0.01 (0.00–0.02), K_2O 17.84 (17.77–17.88), CaO 0.07 (0.03–0.10), B_2O_3 67.21 (66.64–67.76), H_2O_{calc} 13.91, total 99.04. H_2O content was calculated by stoichiometry for $(OH)_2(H_2O)$, according to structural data.

The empirical formula calculated on the basis of 10 O atoms per formula unit is $K_{0.98}B_{5.005}O_7(OH)_2{\cdot}H_2O$. The idealised formula is $KB_5O_7(OH)_2{\cdot}H_2O$ which requires K_2O 18.31, B_2O_3 67.68, H_2O 14.01, total 100 wt.%.

X-ray crystallography

Powder X-ray diffraction (XRD) data of yarzhemskiite (Table 1) were collected with a Rigaku R-AXIS Rapid II diffractometer (X-Ray Diffraction Resource Center, St. Petersburg State University, St. Petersburg, Russia) 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 10 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). Parameters for the monoclinic unit cell calculated from the powder data are: $a = 9.473(3)$, $b = 7.521(2)$, $c = 11.422(3)$ Å, $\beta = 97.37(3)°$ and $V = 807.0(7)$ Å^3.

Single-crystal XRD studies of yarzhemskiite were carried out using an Xcalibur S diffractometer (Faculty of Geology, Moscow State University) equipped with a CCD detector. A full sphere of three-dimensional data was collected. The data were corrected for Lorentz and polarisation effects. The crystal structure was

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

I_{obs}	I_{calc}*	d_{obs}	d_{calc}**	*h k l*
86	**79**	**9.39**	**9.397**	**100**
3	2	6.26	6.265	011
3	2	5.867	5.871	110
9	7	5.387	5.390	$\bar{1}$11
5	4	5.049	5.052	111
41	**35**	**4.696**	**4.698**	**200**
8	7	4.523	4.524	012
6	6	4.247	4.248	$\bar{1}$12
13	12	3.982	3.984	210
13	11	3.922	3.924	112
7	6	3.867	3.866	$\bar{2}$02
17	24	3.759	3.760	020
6	8	3.567	3.569	021
3	2	3.436	3.438	$\bar{2}$12
13	14, 3	3.379	3.381, 3.374	$\bar{1}$21, 013
18	**17, 2**	**3.296**	**3.297, 3.293**	**$\bar{1}$13, 121**
19	**12, 8**	**3.130**	**3.133, 3.132**	**022, 300**
16	15	3.107	3.105	212
3	3	3.067	3.067	113
42	**50**	**2.935**	**2.936**	**220**
100	**12, 2, 100, 8**	**2.898**	**2.902, 2.901, 2.898, 2.891**	**$\bar{3}$02, $\bar{2}$13, $\bar{2}$21, 310**
56	**51**	**2.832**	**2.832**	**004**
8	10	2.789	2.789	221
3	2	2.723	2.726	311
11	12	2.696	2.695	$\bar{2}$22
4	3	2.649	2.650	014
12	6, 10	2.621	2.626, 2.621	$\bar{1}$23, 104
12	10, 2	2.606	2.604, 2.604	302, 213
6	8	2.505	2.505	123
7	9	2.422	2.422	130
12	3, 9, 5	2.407	2.412, 2.407, 2.402	$\bar{2}$23, 320, $\bar{3}$21
3	3	2.308	2.309	321
14	3, 10, 6	2.251	2.254, 2.252, 2.248	$\bar{1}$32, $\bar{4}$11, $\bar{3}$04
4	3, 3	2.202	2.201, 2.199	132, 214
11	2, 7, 4	2.173	2.177, 2.172, 2.169	$\bar{4}$12, $\bar{1}$15, 015
16	13, 2, 4, 7	2.149	2.150, 2.150, 2.147, 2.141	411, 124, 231, 322
9	11, 2	2.126	2.126, 2.124	$\bar{3}$23, $\bar{2}$24
6	10	2.104	2.103	$\bar{2}$32
3	3, 2	2.077	2.078, 2.070	402, $\bar{1}$33
5	5	2.060	2.059	115
12	16	2.040	2.040	$\bar{4}$13
11	20	2.020	2.020	232
7	9	2.004	2.003	412
3	4	1.979	1.979	304
8	8, 5	1.962	1.962, 1.960	224, -233
2	2	1.929	1.929	$\bar{3}$24
2	2	1.914	1.914	314
18	**4, 22, 2, 5**	**1.867**	**1.872, 1.867, 1.861, 1.860**	**$\bar{4}$14, $\bar{2}$25, 125, 233**
2	2	1.832	1.831	016
2	2	1.796	1.796	$\bar{2}$34
2	2	1.766	1.766	511
4	5	1.753	1.751	324
2	2	1.739	1.740	142
2	2	1.718	1.716	$\bar{3}$06
2	2	1.691	1.695	234
2	3	1.668	1.666	$\bar{5}$04
2	3, 2	1.613	1.614, 1.611	$\bar{2}$43, $\bar{3}$41
1	2	1.606	1.605	$\bar{5}$23
2	4	1.594	1.593	$\bar{1}$17
2	2, 2, 3	1.487	1.491, 1.486, 1.485	$\bar{5}$32, $\bar{6}$13, 150
2	2, 2	1.470	1.471, 1.468	$\bar{4}$41, 440
3	2, 2, 3	1.447	1.449, 1.449, 1.447	$\bar{4}$42, 343, 045
2	2, 2, 2	1.415	1.418, 1.415, 1.413	532, $\bar{2}$45, 621
1	2	1.409	1.408	$\bar{3}$27
2	5	1.397	1.397	053
1	2	1.389	1.388	406
2	5	1.334	1.334	$\bar{5}$41

*For the calculated pattern, only reflections with intensities ≥2 are given (for ≥1 see supplementary material); **for the unit-cell parameters calculated from single-crystal data; the strongest reflections are marked in boldtype.

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

Crystal data	
Formula	$KB_5O_7(OH)_2{\cdot}H_2O$
Crystal size (mm)	0.19 × 0.26 × 0.27
Crystal system, space group	Monoclinic, $P2_1/c$
Formula weight	257.18
Temperature (K)	293(2)
a, *b*, *c* (Å)	9.47340(18), 7.52030(16), 11.4205(2)
β (°)	97.3002(17)
V (Å^3)	807.03(3)
Z	4
Absorption coefficient μ (mm^{-1})	0.699
Data collection	
Diffractometer	Xcalibur S CCD
Radiation, wavelength (Å)	Mo*K*α, 0.71073
F_{000}	512
θ range for data collection (°) / collection mode	3.25–30.50 / full sphere
Index ranges	$-13 \le h \le 13$, $-10 \le k \le 10$, $-16 \le l \le 16$
Reflections collected	15,711
Independent reflections	2464 ($R_{int} = 0.0442$)
Independent reflections with $I > 2\sigma(I)$	2220
Refinement	
Data reduction	*CrysAlisPro* (Agilent Technologies, 2014)
Absorption correction	Multi-scan. Empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	162
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0336$, w$R_2 = 0.0711$
R indices (all data)	$R_1 = 0.0394$, w$R_2 = 0.0737$
GoF	1.111
Largest diff. peak and hole (e^-/Å^3)	0.31 and –0.48

solved by direct methods and refined using the *SHELX-97* software package (Sheldrick, 2015) to $R = 0.0336$ for 2220 unique reflections with $I > 2\sigma(I)$. The H atoms of OH groups and H_2O molecule were localised from the difference-Fourier synthesis. Crystal data, data collection information and structure refinement details are presented in Table 2, atom coordinates and displacement parameters in Table 3 and 4, selected interatomic distances in Table 4, data on hydrogen-bond geometry in Table 5 and bond-valence calculations in Table 6. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Discussion

The crystal structure of yarzhemskiite $K[B_5O_7(OH)_2]{\cdot}H_2O$ (Fig. 4), as well as its synthetic analogue (Zhang *et al.*, 2005) and the isostructural mineral larderellite $(NH_4)[B_5O_7(OH)_2]{\cdot}H_2O$ (Merlino and Sartori, 1969), is based on the infinite chains built by boron-centred polyhedra, which are running along the *b* axis (Fig. 5*a*). The basic structural unit of the chain is a double ring $B_5O_7(OH)_2$ consisting of one BO_4 tetrahedron and four BO_3 triangles; within the chain, each unit is linked with the adjacent one through the 2_1 symmetry operation. K^+ cations centre ten-fold polyhedra which form, together with the borate chains $[B_5O_7(OH)_2]^-_\infty$, layers parallel to (100) (Fig. 5*b*,*c*). Adjacent layers

Table 3. Coordinates, equivalent and anisotropic displacement parameters (U_{eq}, in Å^2) of atoms in yarzhemskiite.

Site	*x*	*y*	*z*	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	0.32672(4)	0.43043(5)	0.26804(3)	0.02495(10)	0.02385(17)	0.0306(2)	0.02016(17)	−0.00889(13)	0.00179(12)	0.00104(14)
B(1)	0.56696(15)	0.3086(2)	0.06854(13)	0.0111(3)	0.0105(6)	0.0114(6)	0.0116(6)	−0.0008(5)	0.0018(5)	0.0004(5)
B(2)	0.74642(15)	0.5204(2)	0.03927(13)	0.0122(3)	0.0113(6)	0.0134(7)	0.0119(6)	0.0004(5)	0.0015(5)	−0.0012(5)
B(3)	0.70120(15)	0.4510(2)	0.24462(12)	0.0123(3)	0.0126(6)	0.0147(7)	0.0094(6)	−0.0004(5)	0.0007(5)	−0.0006(5)
B(4)	0.63126(15)	0.5931(2)	0.42519(12)	0.0113(3)	0.0109(6)	0.0115(6)	0.0116(6)	0.0003(5)	0.0018(5)	0.0009(5)
B(5)	0.82576(16)	0.3889(2)	0.44642(13)	0.0121(3)	0.0122(6)	0.0117(7)	0.0125(6)	0.0005(5)	0.0018(5)	0.0010(5)
O(1)	0.45849(10)	0.19876(13)	0.01776(8)	0.01315(19)	0.0130(4)	0.0150(5)	0.0115(4)	−0.0003(3)	0.0018(3)	−0.0046(4)
O(2)	0.63832(10)	0.40612(13)	−0.00853(8)	0.0135(2)	0.0142(4)	0.0169(5)	0.0094(4)	−0.0002(3)	0.0015(3)	−0.0051(4)
O(3)	0.81700(11)	0.60402(14)	0.95840(9)	0.0171(2)	0.0168(5)	0.0221(5)	0.0126(4)	0.0006(4)	0.0026(4)	−0.0093(4)
H(3)	0.8894(16)	0.666(3)	0.9841(18)	0.040(6)*						
O(4)	0.60320(10)	0.31809(13)	0.18617(8)	0.0154(2)	0.0180(5)	0.0179(5)	0.0103(4)	0.0002(4)	0.0021(3)	−0.0072(4)
O(5)	0.77458(10)	0.54786(13)	0.15724(8)	0.0144(2)	0.0147(4)	0.0183(5)	0.0100(4)	0.0003(3)	0.0013(3)	−0.0054(4)
O(6)	0.61882(10)	0.57767(13)	0.30691(8)	0.0147(2)	0.0157(4)	0.0185(5)	0.0094(4)	−0.0005(4)	−0.0001(3)	0.0061(4)
O(7)	0.80982(10)	0.36331(14)	0.32830(8)	0.0146(2)	0.0146(4)	0.0180(5)	0.0110(4)	−0.0009(4)	0.0012(3)	0.0057(4)
O(8)	0.73337(10)	0.50008(13)	0.49835(8)	0.0135(2)	0.0144(4)	0.0169(5)	0.0088(4)	−0.0004(3)	0.0001(3)	0.0058(4)
O(9)	0.93297(11)	0.30529(15)	0.51540(9)	0.0186(2)	0.0174(5)	0.0244(5)	0.0133(5)	−0.0009(4)	−0.0011(4)	0.0095(4)
H(9)	0.934(2)	0.336(3)	0.5864(10)	0.043(6)*						
O(10)	0.94258(12)	0.09249(16)	0.23519(9)	0.0232(2)	0.0215(5)	0.0311(6)	0.0166(5)	−0.0033(4)	0.0006(4)	0.0096(5)
H(10A)	0.912(2)	0.175(2)	0.2760(16)	0.040(6)*						
H(10B)	1.0240(14)	0.062(3)	0.2680(19)	0.052(7)*						

*U_{iso}. The positions of H atoms were localised from the difference-Fourier map and refined with O–H and H–H distances softly restrained to 0.85(1) and 1.37(2) Å, respectively, to hold near-optimal geometry.

Table 4. Selected interatomic distances (Å) in the structure of yarzhemskiite.

K–O(3)	2.7774(10)	B(1)–O(4)	1.3456(17)	B(3)–O(4)	1.4659(17)
K–O(10)	2.8234(12)	B(1)–O(2)	1.3860(17)	B(3)–O(7)	1.4687(17)
K–O(8)	2.8463(9)	B(1)–O(1)	1.3867(17)	B(3)–O(6)	1.4710(17)
K–O(6)	2.8545(11)	<B(1)–O>	1.373	B(3)–O(5)	1.4785(17)
K–O(6)	2.9611(11)			<B(3)–O>	1.471
K–O(4)	3.0116(11)	B(2)–O(5)	1.3556(17)		
K–O(4)	3.0208(11)	B(2)–O(3)	1.3612(17)	B(4)–O(6)	1.3459(16)
K–O(1)	3.1194(10)	B(2)–O(2)	1.3939(17)	B(4)–O(8)	1.3847(16)
K–O(5)	3.1835(11)	<B(2)–O>	1.370	B(4)–O(1)	1.3856(17)
K–O(2)	3.2640(10)			<B(4)–O>	1.372
<K–O>	2.986	B(5)–O(7)	1.3520(17)		
		B(5)–O(9)	1.3580(17)		
		B(5)–O(8)	1.3959(17)		
		<B(5)–O>	1.369		

Table 5. Hydrogen-bond geometry (Å,°) in the structure of yarzhemskiite.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	∠(*D*–H···*A*)
O(3)–H(3)···O(9)	0.849(10)	1.983(12)	2.7948(14)	160(2)
O(9)–H(9)···O(10)	0.843(9)	1.773(10)	2.6156(15)	177(2)
O(10)–H(10A)···O(7)	0.847(9)	1.859(10)	2.6835(15)	164(2)
O(10)–H(10B)···O(5)	0.845(9)	1.992(11)	2.8222(14)	167(2)

are linked only *via* H bonds resulting in the perfect {100} cleavage of the mineral.

According to the classification of fundamental building blocks (*FBB*) in borates, yarzhemskiite, as well as larderellite, contains the following *FBB*: 4Δ1□:<2Δ1□>–<2Δ1□>. This code means that four B-centred triangles (Δ) and one B-centred tetrahedron (□) form a cluster consisting of two borate rings <2Δ1□> linked *via* the tetrahedron belonging to both rings (Burns *et al.*, 1995; Grice *et al.*, 1999). The symmetry of this borate fragment is $\bar{4}m2$ (Belokoneva, 2005). In yarzhemskiite and larderellite these *FBB*s are connected *via* common O vertices to form chains $[B_5O_7(OH)_2]^{n-}{}_n$ (Fig. 5*a*). In other minerals such *FBB* occurs as the isolated pentaborate ion $[B_5O_6(OH)_4]^-$, namely in santite $K[B_5O_6(OH)_4]{\cdot}2H_2O$ (Zachariasen and Plettinger, 1963; Merlino and Sartori, 1970), sborgite $Na[B_5O_6(OH)_4]{\cdot}3H_2O$ (Merlino and Sartori, 1972), ramanite-(Cs) $Cs[B_5O_6(OH)_4]{\cdot}2H_2O$ and ramanite-(Rb), $Rb[B_5O_6(OH)_4]{\cdot}2H_2O$ (Behm, 1984; Penin *et al.*, 2002; Thomas *et al.*, 2008). In ammonioborite $(NH_4)_3[B_{15}O_{20}(OH)_8]{\cdot}4H_2O$ (Merlino and Sartori, 1971), three units $B_5O_6(OH)_4^-$ are connected to form the anion $[B_{15}O_{20}(OH)_8]^{3-}$ with *FBB* = 12Δ3□:3(<2Δ1□>–<2Δ1□>) (Grice *et al.*, 1999).

Yarzhemskiite $K[B_5O_7(OH)_2]{\cdot}H_2O$ and larderellite $(NH_4)[B_5O_7(OH)_2]{\cdot}H_2O$ (Table 7) are isostructural, however, there is no evidence that they form a solid-solution series. Larderellite does not contain admixed potassium (Palache *et al.*, 1951; Anthony *et al.*, 2003) and our electron-microprobe and IR spectroscopy data show the absence of ammonium in a detectable amount in yarzhemskiite. The crystal structures of these minerals and the synthetic analogue of yarzhemskiite are very close in character to B-centred polyhedra. Mean <B–O> distances vary from 1.369 to 1.373 Å for BO_3 triangles and 1.471 Å for tetrahedra in yarzhemskiite; the corresponding values are 1.36–1.38 and 1.47 Å in larderellite (Merlino and Sartori, 1969) and 1.364–1.372 and 1.470 Å in the synthetic analogue of yarzhemskiite (Zhang *et al.*, 2005). Potassium cations in yarzhemskiite and its synthetic analogue are ten-coordinated. K–O distances vary from 2.777 to 3.264 Å (mean <K–O> 2.986 Å) in yarzhemskiite and from 2.775 to 3.267 Å (mean <K–O> 2.987 Å) in synthetic $K[B_5O_7(OH)_2]{\cdot}H_2O$ while ammonium cations in larderellite occupy larger ten-fold polyhedra with NH_4–O distances varying from 2.86 to 3.35 Å with a mean <NH_4–O> distance of 3.07 Å. This results in the larger values of the unit-cell dimensions and volume of larderellite [V = 835.4 Å^3] (Merlino and Sartori, 1969) compared with those in yarzhemskiite [807.0 Å^3] and its synthetic analogue [807.2 Å^3] (Zhang *et al.*, 2005).

Yarzhemskiite differs from structurally related larderellite and chemically related santite (Table 7) in the genetic aspect. Both larderellite and santite were first discovered at Larderello, Tuscany, Italy in hot lagoons where boron-rich volcanic fumaroles meet with water (Bechi, 1854; Palache *et al.*, 1951;

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Table 6. Bond-valence calculations for yarzhemskiite.

	K	B(1)	B(2)	B(3)	B(4)	B(5)	Σ	H bonding	Σ
O(1)	0.07	0.96			0.96		1.99		1.99
O(2)	0.05	0.96	0.94				1.95		1.95
O(3) = OH	0.17		1.03				1.20	−0.19[O(9)]	1.01
O(4)	0.09	1.07		0.77			2.02		2.02
	0.09								
O(5)	0.06		1.04	0.75			1.85	+0.18[O(10)]	2.03
O(6)	0.14			0.76	1.07		2.08		2.08
	0.11								
O(7)				0.77		1.05	1.82	+0.24 [O(10)]	2.06
O(8)	0.14				0.96	0.93	2.03		2.03
O(9) = OH						1.04	1.04	+0.19[O(3)]−0.28[O(10)]	0.95
O(10) = H_2O	0.15						0.15	+0.28[O(9)]−0.24[O(7)]−0.18[O(5)]	0.01
Σ	1.07	2.99	3.01	3.05	2.99				

Bond-valence parameters for the K–O and B–O bonds were taken from (Brese and O'Keeffe, 1991) and those for H bonding from (Ferraris and Ivaldi, 1988).

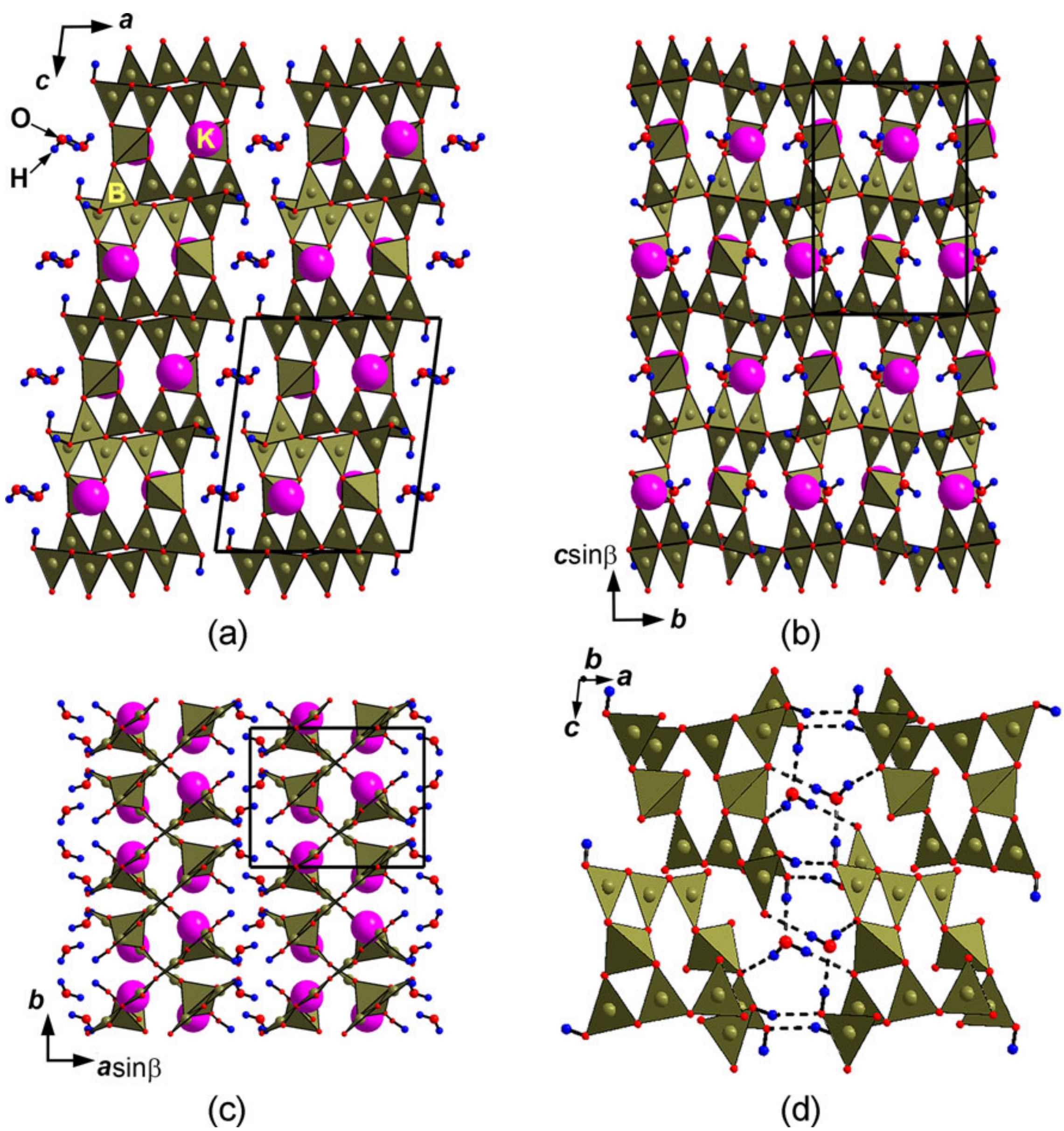

Fig. 4. The crystal structure of yarzhemskiite in three projections with the outlined unit cell (*a*, *b*, *c*) and the fragment of the structure with shown H-bonding scheme (*d*). Key shown in (a).

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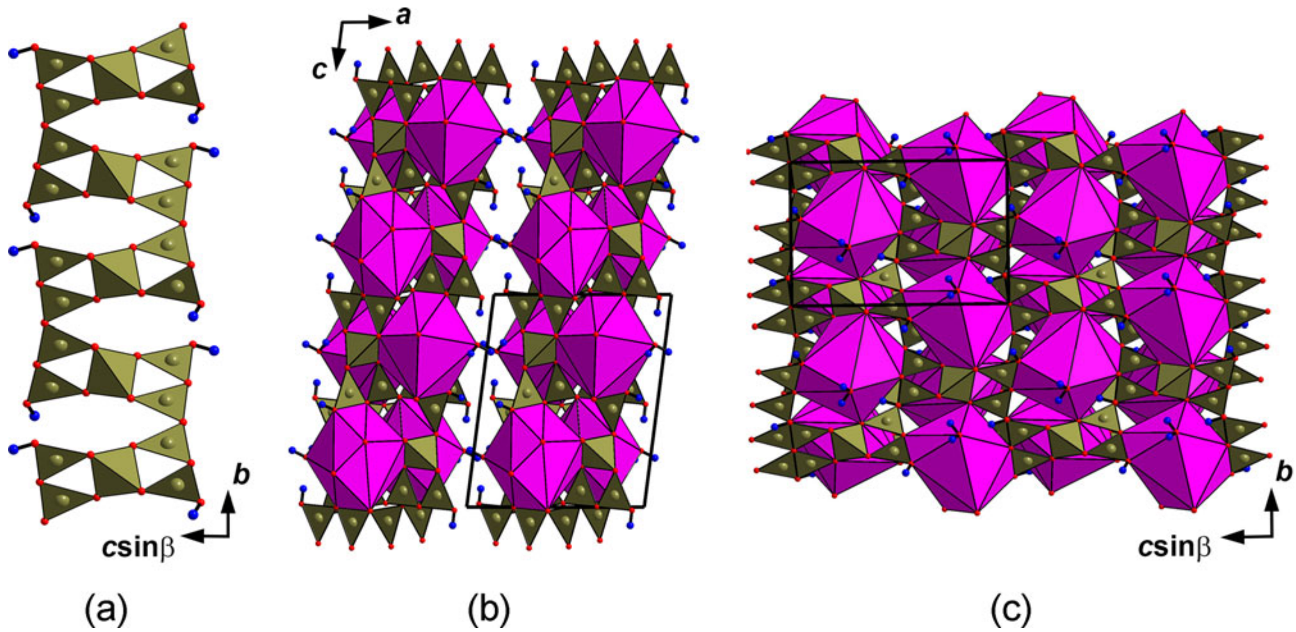

Fig. 5. Infinite chain built by BO_3 triangles and BO_4 tetrahedra (*a*) and the layers formed by these chains and ten-fold K-centred polyhedra (*b*, *c*) in the structure of yarzhemskiite. The unit cell is outlined in (*b*, *c*). For legend see Fig. 4.

Table 7. Comparative data for yarzhemskiite, larderellite and santite.

Mineral	Yarzhemskiite	Larderellite	Santite**
Formula	$K[B_5O_7(OH)_2]·H_2O$	$(NH_4)[B_5O_7(OH)_2]·H_2O$	$K[B_5O_6(OH)_4]·2H_2O$
Crystal system, Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$*	Orthorhombic, *Aba*2
Unit-cell data:			
a (Å)	9.4734	9.447–9.47	11.10
b (Å)	7.5203	7.615–7.63	11.18
c (Å)	11.4205	11.63–11.65	9.08
β (°)	97.300	96.75–97.08	
V ($Å^3$)	807.0	830.9–835.4	1127
Z	4	4	4
Strongest reflections of the	9.39–86	9.45–50	5.60–70
powder XRD pattern: *d*, Å – *I*	4.696–41	4.70–100	3.52–85
	2.935–42	2.960–71	3.36–100
	2.898–100	2.921–100	3.28–20
	2.832–56	2.887–100	2.767–30
Optical data:			
α	1.484	1.493	1.422
β	1.508	1.509	1.435
γ	1.544	1.561	1.480
Optical sign, 2V	+75°	+58°	+70°
Sources	This work	Palache *et al.* (1951); Merlino and Sartori (1969); Anthony *et al.* (2003)	Clark and Christ (1959); Merlino and Sartori (1970); Anthony *et al.* (2003)

*Given here in standard setting; original data were reported by Merlino and Sartori (1969) for space group $P2_1/a$ and, therefore, for unit cell with changed *c* and *a* parameters.
**Powder XRD data are given for the synthetic analogue of santite studied by Clark and Christ (1959).

Merlino and Sartori, 1970). Later both these minerals were found in deposits of moderately hot fumaroles at the Vulcano island, Aeolian Archipelago, Sicily, Italy (Campostrini *et al.*, 2011). Santite is also mentioned, in association with Na, Ca and Mg borates, in deposits of the thermal spring at Eagle Borax Spring, Death Valley, California, USA (Crowley, 1996; Anthony *et al.*, 2003), and as a daughter phase in fluid inclusions in minerals of boron-enriched granitic pegmatites from three localities: Il Prado pegmatite, San Piero in Campo, Elba Island, Italy (Thomas *et al.*, 2008) and the Vezdarinskaya and Leskhozovskaya pegmatite veins, Shakhdara River, SW Pamirs, Tajikistan (Smirnov, 2015). Thus, larderellite and santite in all known cases were deposited from the hot gas or hot water solutions. Unlike them, yarzhemskiite was formed as a result of diagenetic or post-diagenetic processes in boron-bearing evaporites (see: Yarzhemskii, 1984).

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