Khvorovite, Pb₄²⁺Ca₂[Si₈B₂(SiB)O₂₈]F, a new hyalotekite-group mineral from the Darai-Pioz alkaline massif, Tajikistan: Description and crystal structure

LEONID A. PAUTOV¹, ATALI A. AGAKHANOV^{1,2}, ELENA SOKOLOVA^{3,*}, FRANK C. HAWTHORNE³, VLADIMIR Y. KARPENKO¹, OLEG I. SIIDRA², VIKTOR K. GARANIN¹ AND YASSIR A. ABDU³

¹ Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Pr-kt, 18-2, 119071 Moscow, Russia

³ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

[Received 6 November 2014; Accepted 8 January 2015; Associate Editor: S. Krivovichev]

ABSTRACT

Khvorovite, ideally $Pb_4^{2+}Ca_2[Si_8B_2(SiB)O_{28}]F$, is a new borosilicate mineral of the hyalotekite group from the Darai-Pioz alkaline massif in the upper reaches of the Darai-Pioz river, Tajikistan. Khvorovite was found in a pectolite aggregate in silexites (quartz-rich rocks). The pectolite aggregate consists mainly of pectolite, quartz and fluorite, with minor aegirine, polylithionite, turkestanite and baratovite; accessory minerals are calcite, pyrochlore-group minerals, reedmergnerite, stillwellite-(Ce), pekovite, zeravshanite, senkevichite, sokolovaite, mendeleevite-(Ce), alamosite, orlovite, leucosphenite and several unknown Cs-silicates. Khvorovite occurs as irregular grains, rarely with square or rectangular sections up to 150 µm, and grain aggregates up to 0.5 mm. Khvorovite is colourless, rarely white, transparent with a white streak, has a vitreous lustre and does not fluoresce under ultraviolet light. Cleavage and parting were not observed. Mohs hardness is 5-5.5, and khvorovite is brittle with an uneven fracture. The measured and calculated densities are 3.96(2) and 3.968 g/cm³, respectively. Khvorovite is biaxial (+) with refractive indices ($\lambda = 589$ nm) $\alpha = 1.659(3)$, $\beta_{calc.} = 1.671(2)$, $\gamma =$ 1.676(3); $2V_{\text{meas.}} = 64(3)^{\circ}$, medium dispersion: r < v. Khvorovite is triclinic, space group $I\overline{I}$, a =11.354(2), b = 10.960(2), c = 10.271(2) Å, $\alpha = 90.32(3)$, $\beta = 90.00(3)$, $\gamma = 90.00(3)^\circ$, V = 1278(1) Å³, Z = 2. The six strongest lines in the powder X-ray diffraction pattern [d (Å), I, (hkl)] are: 7.86, 100, (110); 7.65, 90, (101); 7.55, 90, (011); 3.81, 90, (202); 3.55, 90, (301); 2.934, 90, (312, 312). Chemical analysis by electron microprobe gave SiO₂ 36.98, B₂O₃ 6.01, Y₂O₃ 0.26, PbO 40.08, BaO 6.18, SrO 0.43, CaO 6.77, K₂O 1.72, Na₂O 0.41, F 0.88, O=F -0.37, sum 99.35 wt.%. The empirical formula based on 29 (O+F) a.p.f.u. is $(Pb_{2.76}^{2+}Ba_{0.62}K_{0.56}Na_{0.16})_{\Sigma 4.10}(Ca_{1.86}Sr_{0.06}Y_{0.04}Na_{0.04})_{\Sigma 2}$ $[Si_8B_2(Si_{1.46}B_{0.65})_{\Sigma 2.11}O_{28}](F_{0.71}O_{0.29}), Z = 2, and the simplified formula is$ $(Pb^{2+}, Ba, K)_4Ca_2[Si_8B_2(Si_8B_2O_{28}]F]$. The crystal structure of khvorovite was refined to $R_1 = 2.89\%$ based on 3680 observed reflections collected on a four-circle diffractometer with MoK α radiation. In the crystal structure of khvorovite, there are four [4]-coordinated Si sites occupied solely by Si with $\langle Si-O \rangle = 1.617$ Å. The [4]-coordinated B site is occupied solely by B, with $\langle B-O \rangle = 1.478$ Å. The [4]-coordinated T site is occupied by Si and B (Si_{1.46}B_{0.54}), with $\langle T-O \rangle = 1.605$ Å; it ideally gives (SiB) a.p.f.u. The Si, B and T tetrahedra form an interrupted framework of ideal composition $[Si_8B_2(SiB)O_{28}]^{11-}$. The interstitial cations are Pb²⁺, Ba and K (minor Na) [A(11-22) sites] and Ca [M site]. The two A sites are each split into two subsites ~0.5 Å apart and occupied by Pb^{2+} and Ba + K.

* E-mail: elena_sokolova@umanitoba.ca DOI: 10.1180/minmag.2015.079.4.06

² Department of Crystallography, St. Petersburg State University, University Embankment 7/9, 119034 St. Petersburg, Russia

The [8]-coordinated *M* site is occupied mainly by Ca, with minor Sr, Y and Na. Khvorovite is a Pb²⁺analogue of hyalotekite, $(Ba,Pb^{2+},K)_4(Ca,Y)_2[Si_8(B,Be)_2(Si,B)_2O_{28}]F$ and a Pb²⁺-, Ca-analogue of kapitsaite-(Y), $(Ba,K)_4(Y,Ca)_2[Si_8B_2(B,Si)_2O_{28}]F$. It is named after Pavel V. Khvorov (b. 1965), a Russian mineralogist, to honour his contribution to the study of the mineralogy of the Darai-Pioz massif.

Keywords: khvorovite, new mineral species, silicate, alkaline rocks, Darai-Pioz massif, Tajikistan, hyalotekite, electron microprobe analysis, crystal structure.

Introduction

KHVOROVITE occurs in the moraine of the Darai-Pioz glacier in the upper reaches of the Darai-Pioz River, the Alaisky mountain ridge, Tien-Shan Mountains, Tajikistan. The mineral is named khvorovite after Pavel Vitalyevich Khvorov (Павел Витальевич Хворов) (b. 1965), а Russian mineralogist who made major contributions to the mineralogy of the Darai-Pioz massif and was the first to describe hyalotekite from there and study its optical properties (Khvorov, pers. comm., 1992). The new mineral species and its name were approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification, (IMA 2014-050). The holotype specimen has been deposited in the mineral collection of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, registration # 4573/1. We describe here this new Pb^{2+} borosilicate and report its crystal structure.

Review of the relevant literature

Khvorovite, ideally Pb₄²⁺Ca₂[Si₈B₂(SiB)O₂₈]F, is a Pb²⁺-analogue of hyalotekite, (Ba,Pb²⁺,K)₄ $(Ca, Y)_{2}[Si_{8}(B, Be)_{2}(Si, B)_{2}O_{28}]F$ and a Pb^{2+} , Caanalogue of kapitsaite-(Y), $(Ba,K)_4(Y,Ca)_2$ [Si₈B₂(B,Si)₂O₂₈]F (Table 1). Hyalotekite was first described by Nordenskiöld (1877) as a lead silicate from Långban, Värmland, Sweden. Lindström (1887) reported a more complete chemical analysis of the holotype material that revealed Ba and Pb²⁺ as well as Be and B. In both original analyses of the holotype hyalotekite. Ba > Pb^{2+} (Table 2). The empirical formula of hyalotekite based on the chemical analysis of Lindström (1887) and calculated on 29 (O+F) anions is as follows $(Ba_{1.96}Pb_{1.68}^{2+}K_{0.28}Na_{0.08})_{\Sigma 4}$ $(Ca_{2.08}Mn_{0.06}Mg_{0.03}Cu_{0.02})_{\Sigma 2.19}(Si_{9.82}B_{1.60})$ $Be_{0.45}Al_{0.05}Fe_{0.01}^{3+})_{\Sigma 11.93}O_{28,20}F_{0.78}Cl_{0.03}, Z = 2$ (see Table 2). Moore et al. (1982) solved the crystal structure of hyalotekite. Christy et al.

(1998) used the single-crystal X-ray diffraction (XRD) data of Moore *et al.* (1982) to refine the crystal structure of hyalotekite and revise its structural formula. Grew *et al.* (1994) described hyalotekite from the Darai-Pioz alkaline massif, Tajikistan (second locality). Pautov *et al.* (2000) described kapitsaite-(Y), (Ba,K)₄(Y,Ca)₂ [Si₈(B,Si)₄O₂₈]F, from the Darai-Pioz alkaline massif, Tajikistan (Tables 1, 2) and Sokolova *et al.* (2000) refined its structure. The current formula of hyalotekite in the IMA list of minerals is as follows (Pb,Ba,K)₄(Ca,Y)₂(B,Be)₂ (Si,B)₂Si₈O₂₈F. This formula is incorrect as holotype hyalotekite has Ba > Pb²⁺.

Occurrence

Khvorovite was found in rocks of the Darai-Pioz alkaline massif (39°30'N 70°40'E), which is located at the intersection of the Turkestansky, Zeravshansky and Alaisky ridges [the Rasht (formerly Garm) district, Tajikistan]. In plan, the Darai-Pioz massif is equant, extended slightly in the northwest direction and occupies $\sim 16 \text{ km}^2$. In the meridional direction, the massif is dissected by a glacial valley and much of the rock is covered by glaciers. The first data on petrography and mineralogy of the Darai-Pioz massif were reported by Moskvin (1937) who took part in the Tajik-Pamir expedition in the 1920-1930s. The unique rare-metal and boron mineralization of the Darai-Pioz massif was described by Dusmatov et al. (1963, 1967a,b), Dusmatov (1968), Semenov et al. (1963, 1973) and Efimov et al. (1970). The geochemistry and mineralogy of the Darai-Pioz massif were described by Dusmatov (1971), Dusmatov et al. (1972), Belakovskiy (1991), Grew et al. (1994) and Reguir et al. (1999). However, the PhD dissertation of Dusmatov (1971) remains the most complete description of the geology, petrography and mineralogy of the Darai-Pioz massif.

The Darai-Pioz massif is a multiphase intrusion and occupies the core of a large synclinal fold of

	Khvorovite	Hyalotekite	Kapitsaite-(Y)
Formula System Space group	Pb ²⁺ Ca ₂ [Si ₈ B ₂ (SiB)O ₂₈]F Triclinic <i>J</i> I	$\begin{array}{l} (Ba,Pb,K)_4(Ca,Y)_2[Si_8(B,Be)_2(Si,B)_2O_{28}]F\\ Triclinic\\ \tilde{J}\end{array}$	$\begin{array}{l} (Ba,K)_4(Y,Ca)_2[Si_8B_2(B,Si)_2O_{28}]F\\ Triclinic\\ IT\\ IT\\ IT\\ IT\\ IT\\ IT\\ IT\\ IT\\ IT\\ IT$
$\begin{array}{c} \begin{array}{c} a \\ a \\ b \\ c \\ c \\ a \\ c \\ d \end{array} \end{array}$	11.353(2) 10.960(2) 10.271(2) 90.37(3)	11.310(2) 10.955(2) 10.317(3) 90.43(7)	11.181(4) 10.850(7) 10.252(4) 90.64(6)
$ \begin{array}{c} \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	90.00(3) 90.00(3) 1278(1) 2	90.02(2) 90.16(2) 1278.3(7) 2	90.05(4) 89.97(7) 1243.6(9) 2
$D_{\text{meas}}/D_{\text{calc}}$ (g cm ⁻³) Strongest reflections in the powder data d_{meas} (Å) (I) Optical character α	3.96/3.968 7.86(10), 7.65(9), 7.55(9), 3.81(9), 3.55(9), 2.934(9), 5.15(8) Biaxial (+) 1.659 1.671	3.81–3.82/3.83 3.45(100), 3.53(80), 2.94(80), 3.81(70), 2.297(65), 2.143(65), 7.7(60) Biaxial (+) 1.646–1.656 1.649–1.660 1.649–1.670	3.74/3.79 3.77(100), 2.90(90), 2.93(80), 3.24(75), 7.80(70), 3.73(70), 2.74(65) Biaxial (+) 1.624 1.624 1.628
22 _{meas.} / _{calc.} (°) Colour	64/- White	57-60.555.4-62.5 White to pearly-grey	69/67.7 Light-rosy
* Although the hvalotekite gro	up has not been approved officially by the	CNMNC IMA. the work on the definition of the arc	oup is under way. Data are from this work

TABLE 1. Hyalotekite-group minerals*.

for knorovite; PDF-2 # 019-0572, Grew *et al.* (1994), Christy *et al.* (1998) and Moore *et al.* (1982) for hyalotekite and Pautov *et al.* (2000) and Sokolova *et al.* (2000) for knorovite; PDF-2 # 019-0572, Grew *et al.* (1994), Christy *et al.* (1998) and Moore *et al.* (1982) for hyalotekite and Pautov *et al.* (2000) and Sokolova *et al.* (2000) for knorovite; PDF-2 # 019-0572, Grew *et al.* (1994), Christy *et al.* (1998) and Moore *et al.* (1982) for hyalotekite and Pautov *et al.* (2000) and Sokolova *et al.* (2000)

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Constituent	——— Hyalo	tekite ——	Kapitsaite-(Y) ³
	Nordenskiöld ¹ (1877)	Lindström*,2 (1887)	Pautov et al. (2000)
SiO ₂	39.62	39.47	34.98
$REE_2O_3^{**}$			2.85
Y_2O_3			7.93
Fe ₂ O ₃		0.06	
Al_2O_3	little	0.18	0.04
B_2O_3		3.73	8.68
PbO	25.30	25.11	1.95
BaO	20.66	20.08	38.18
CuO		0.09	
FeO			0.01
MnO		0.29	0.05
CaO	7.00	7.82	3.12
MgO		0.09	
BeO		0.75	
K ₂ O	little	0.89	0.87
Na ₂ O		0.17	0.46
Cl		0.06	0.01
F		0.99	1.40
L.O.I.	0.82	0.59	
Total	93.40	100.37	100.53
O=Cl		-0.01	0
O=F		-0.42	-0.59
Total	93.40	99.94	99.94

TABLE 2. Chemical analyses for holotype hyalotekite (Långban) and kapitsaite-(Y) (Darai-Pioz).

* Taken from Moore et al. (1982);

** $REE_{2}O_{3}(wt.\%) = La_{2}O_{3} 0.01; Ce_{2}O_{3} 0.09; Pr_{2}O_{3} 0.03; Nd_{2}O_{3} 0.32; Sm_{2}O_{3} 0.36; Gd_{2}O_{3} 0.64; Dy_{2}O_{3} 0.70; Ho_{2}O_{3} 0.14; Er_{2}O_{3} 0.36; Yb_{2}O_{3} 0.20; empirical formulae calculated on 29 (O + F) a.p.f.u., <math>Z = 2$ for hyalotekite: (1) Nordenskiöld (1877): (Ba_{2,31}Pb_{1,4)}^{2+}\Sigma_{4,25}Ca_{2,14}Si_{11,30} O_{29};

(2) Lindström (1887): $(Ba_{1.96}Pb_{1.68}^{2+}K_{0.28}Na_{0.08})_{\Sigma4}(Ca_{2.08}Mn_{0.06}Mg_{0.03}Cu_{0.02})_{\Sigma2.19}$

 $(Si_{9.82}B_{1.60}Be_{0.45}Al_{0.05}Fe_{0.01}^{3+})_{\Sigma 11.93}O_{28.20}F_{0.78}Cl_{0.03};$

 $\begin{array}{l} (3) \ \text{kapitsaite-(Y):} \ (Ba_{3.55}K_{0.26}Pb_{0.12}^{2+}Na_{0.07})_{\Sigma 4.00}(Y_{1.00}Ca_{0.79}Na_{0.14}Gd_{0.05}Dy_{0.05}Nd_{0.03}Sm_{0.03}Er_{0.03}Ce_{0.01}Ho_{0.01} \\ Yb_{0.01})_{\Sigma 2.15}(Si_{7.99}Al_{0.01})_{\Sigma 8.00}(B_{3.55}Si_{0.30})_{\Sigma 3.85}O_{27.95}F_{1.05}. \end{array}$

Carboniferous (Pennsylvanian series) slates. Of particular importance are rocks of the Alaisky (Matchaisky) Upper Paleozoic intrusive complex: an outer ring zone of two-mica tourmaline granites of Late Carboniferous age, an intermediate zone of fine- and medium-grained biotite granites, and a central core of quartz-bearing and quartz-free svenites. To the east, there is a small stock of younger cancrinite-foyaite. Rocks of the massif have been intruded by fine-grained dykes of biotite tourmaline granites and veins of calcite carbonatites and syenite carbonatites are widespread (Faiziev et al., 2010). The principal metasomatic rocks are fenites and baratoviteand miserite-containing quartz-albite-aegirine rocks (Dusmatov, 1971; Semenov et al., 1973;

Reguir et al., 1999). A characteristic feature of the geochemistry of the Darai-Pioz massif is the boron enrichment (Dusmatov et al., 1972), expressed in the widespread occurrence of many borosilicates. Some of them have been described as new mineral species: calcybeborosilite-(Y) (Semenov et al., 1963; Rastsvetaeva et al., 1996; Pekov et al., 2000), tienshanite (Dusmatov et al., 1967a; Malinovskii et al., 1977; Cooper et al., 1998), tadzhikite-(Ce) (Efimov et al., 1970; Chernitsova et al., 1982; Hawthorne et al., 1998), kapitsaite-(Y) (Pautov et al., 2000; Sokolova et al., 2000), pekovite and maleevite (Pautov et al., 2004), byzantievite (Sokolova et al., 2010; Pautov et al., 2011), kirchhoffite (Agakhanov et al., 2012), laptevite-



FIG. 1. General view of quartz-rich rock: pectolite aggregate (1), sogdianite (2), turkestanite (3), aegirine (4). The size of the sample is 12 cm x 9 cm x 5 cm.

(Ce) (Agakhanov *et al.*, 2013; Uvarova *et al.*, 2013). In some pegmatites, reedmergnerite, a boron analogue of albite, is a rock-forming mineral (Dusmatov *et al.*, 1967*b*).

Mineral association

Khyorovite was found in rounded boulders of dominantly medium- and coarse-grained quartz in the moraine of the glacier. Colourless clear quartz is interspersed chaotically with large (up to 10-15 cm) plates of polylithionite, grains of pink or light-orange reedmergnerite, white or pale-green microcline, idiomorphous black crystals of aegirine, violet-red lamellae of sogdianite and sugilite, red-brown lenticular crystals of stillwellite-(Ce) and grass-green crystals of leucosphenite (Fig. 1). In these rocks, the following minerals occur: turkestanite, kapitsaite-(Y), pyrochloregroup minerals, neptunite, galena, eudialyte-group minerals, baratovite, bismuth, sphalerite, fluorite, fluorapatite, calcite and fluorapophyllite. Khvorovite was found in a brown polymineralic aggregate within these boulders. The principal minerals composing this aggregate are pectolite, quartz and Sr-rich fluorite, with minor aegirine, polylithionite, turkestanite and baratovite, and accessory calcite, pyrochlore-group minerals, reedmergnerite, stillwellite-(Ce), pekovite, zeravshanite, senkevichite, sokolovaite, mendeleevite-(Ce), alamosite, orlovite, leucosphenite and a number of unidentified Cs-bearing silicates.

Khvorovite commonly forms irregular grains and polycrystalline aggregates up to $100-150 \ \mu m$ across, rarely grains with sections close to rectangular or square are visible (Figs 2, 3). Khvorovite commonly forms intergrowths with quartz, pectolite, mendeleevite-(Ce), pekovite and alamosite.

Physical properties

Khvorovite is colourless, rarely white, with a vitreous lustre and a white streak. Cleavage and parting were not observed, it is brittle and has uneven fracture. The microhardness of khvorovite is VHN = 620 (with the range of 590-637) which corresponds to Mohs hardness of $5-5\frac{1}{2}$; measurements were performed on the PMT-3, calibrated on NaCl at a loading of 50 g. Khvorovite does not luminesce in short-wave UV-radiation; under the electron beam (U = 20 kV, I = 20 nA), khvorovite fluoresces pale blue. The density, $D_{\text{meas.}} =$ 3.96(2) g/cm³ was determined by flotation in Clerici liquid and $D_{\text{calc.}} = 3.968 \text{ g/cm}^3$ (from the empirical formula). Khvorovite is biaxial (+) with refractive indices ($\lambda = 589 \text{ nm}$) $\alpha = 1.659(3)$, $\beta_{\text{calc.}}$ = 1.671(2), $\gamma = 1.676(3)$. The optical axial angle, measured with a Fedorov stage, is $64(3)^{\circ}$. The β angle was calculated using $2V_{meas.}$ The dispersion is medium, r < v. The compatibility index (1 - Kp/Kc) = 0.016 (for $D_{\text{calc.}} = 3.968 \text{ g/cm}^3$) is rated as superior.

Chemical composition

The chemical composition of khvorovite was determined using a JEOL Superprobe JCXA-733 electron microprobe equipped with an energy-



FIG. 2. Back-scattered electron image of the intergrowth of khvorovite (1), mendeleevite-(Ce) (2), pectolite (3), quartz (4) and pekovite (5).

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FIG. 3. Back-scattered electron image of the intergrowth of khvorovite, pectolite, quartz, pekovite and mendeleevite-(Ce) (a), X-ray maps of the distribution of the specified elements (b-i).

dispersive spectrometer (EDS), an ultrathin ATW2 window, an INCA control system and wavelength-dispersive spectrometers (WDS) (Fersman Mineralogical Museum). For all elements except boron, measurements were carried out using EDS with an accelerating voltage of 20 kV, a specimen current of 2 nA and a beam diameter of 5 µm. Boron was analysed by WDS (STE crystal, an accelerating voltage of 10 kV, a specimen current of 100 nA and a beam diameter of 10-20 µm). In the differential mode of the discriminator, the intensity of $BK\alpha$ was determined by peak area. The following standards were used: USNM 143966 microcline (Si,K), Y2O3 (Y), PbTiO3 (Pb), BaSO₄ (Ba), SrSO₄ (Sr), anorthite USNM 137041 (Ca), albite (Na), MgF₂ (F) and danburite (B). The data were reduced and corrected by the PAP method of Pouchou and Pichoir (1985). Table 3 gives the chemical composition (which is the mean of ten determinations) and the formula unit based on 29 (O + F) atoms per formula unit (a.p.f.u.). The empirical formula for khvorovite is $(Pb_{2.76}^{2+}Ba_{0.62}K_{0.56}Na_{0.16})\Sigma_{4.10}(Ca_{1.86}Sr_{0.06}Y_{0.04})$ $Na_{0.04})\Sigma_2[Si_8B_2(Si_{1.46}B_{0.65})\Sigma_{2.11}O_{28}](F_{0.71}O_{0.29}),$ Z = 2. The simplified and ideal formulae are $(Pb^{2+}, Ba, K)_4Ca_2[Si_8B_2(Si, B)_2O_{28}]F$ and $Pb_4^{2+}Ca_2[Si_8B_2(SiB)O_{28}]F$, respectively.

Raman spectroscopy

The Raman spectrum of khvorovite (Fig. 4) was collected in back-scattered mode with a HORIBA Jobin Yvon-LabRAM ARAMIS integrated confocal micro-Raman system equipped with a 460 mm focal length spectrograph and a multichannel air-cooled (-70° C) CCD detector (University of Manitoba). A magnification of

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Constituent	Average	Range	Esd.	Unit d	formula
SiO ₂	36.98	36.36-37.78	0.50	Si	9.46
$B_2 O_3$	6.01	5.40-6.10	0.35	В	2.65
Y_2O_3	0.26	0.00 - 0.64	0.15	Y	0.04
PbO	40.08	37.24-42.49	1.34	Pb	2.76
BaO	6.18	4.05-8.96	2.17	Ba	0.62
SrO	0.43	0.00 - 0.86	0.17	Sr	0.06
CaO	6.77	6.01-7.37	0.41	Ca	1.86
K ₂ O	1.72	1.39 - 2.05	0.27	Κ	0.56
Na ₂ O	0.41	0.22 - 0.62	0.14	Na	0.20
F	0.88	0.63-1.10	0.14	F	0.71
Total	99.72				
O=F	-0.37				
Total	99.35	98.65-100.86			

TABLE 3. Chemical analysis (wt.%) and unit formula (a.p.f.u.) for khvorovite.

* The formula was calculated on the basis of 29 (O + F) a.p.f.u., Z = 2.

 $100 \times$ was used with an estimated spot size of ~1 µm, a 1800 gr/mm grating and a 532 nm excitation laser. The wavenumber was calibrated using the 520.7 cm⁻¹ line of elemental Si. Strong Raman peaks are observed at 1017, 531, 425 and 256 cm⁻¹, and medium to low intensity peaks at 1100, 937, 783, 713, 642, 485, 296, 221, 203, 170 and 162 cm⁻¹ (Fig. 4). The peaks at 1100, 1017 and 937 cm⁻¹ are attributed to Si–O and B–O stretches, and those at 783, 713 and 642 cm⁻¹ to

stretching vibrations of Si–O–Si bridges. The peaks at 531, 485 and 425 cm⁻¹ may be assigned to bending vibrational modes of SiO₄ tetrahedra and peaks below 400 cm⁻¹ are mainly due to lattice modes.

Powder X-ray diffraction

Powder XRD data were collected using a Debye-Scherrer camera (D = 114 mm) and FeK α



FIG. 4. The Raman spectrum of khvorovite.

radiation. The powder XRD data for khvorovite are given in Table 4. Unit-cell parameters refined from the powder data are as follows: a = 11.35(2), b = 10.97(3), c = 10.28(3) Å, $\alpha = 90.27(4)$, $\beta =$ 89.97(4), $\gamma = 89.98(4)^{\circ}$, V = 1280(2) Å³.

Crystal structure

Data collection and structure refinement

Single-crystal X-ray data for khvorovite were collected using a Bruker APEX II ULTRA threecircle diffractometer with a rotating-anode generator (MoK α), multilayer optics and an APEX II 4K CCD detector (University of Manitoba). The intensities of 7473 reflections with -16 < h < 16, -15 < k < 15, -14 < l < 14 were measured to $60^{\circ}2\theta$ using 30 s per 0.3° frame. Unit-cell dimensions were determined by least-squares refinement of 9921 reflections with $I > 10\sigma(I)$, and are given in Table 5, together with other miscellaneous information on data collection and structure refinement. An absorption correction

was carried out using the SADABS program (Sheldrick, 2008). All calculations were performed with the Bruker SHELXTL version 5.1 system of programs (Sheldrick, 2008). The crystal-structure refinement of khyorovite was undertaken on a twinned crystal with two components related by the twin matrix (100 010 001). Using atom coordinates of hyalotekite (Moore et al., 1982) as a starting model, the crystal structure was refined in space group $I\overline{1}$ to $R_1 = 2.89\%$, the twin ratio being 0.529(2) : 0.471(2). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson, 1992). The site occupancies for the A, M, T, B and Si sites were refined with the scattering parameters of Pb + Ba, Ca, Si, B and Si. Final atom coordinates and anisotropic-displacement parameters are listed in Table 6, selected interatomic distances and framework angles are given in Table 7, and refined sitescattering and assigned site-populations for selected cation sites are given in Table 8. Observed and calculated structure factors and a

							0				
I _{obs.}	$d_{\rm obs.}$ (Å)	$d_{\text{calc.}}$ (Å)	h	k	l	I _{obs.}	$d_{\rm obs.}$ (Å)	$d_{\text{calc.}}$ (Å)	h	k	l
10	7.86	7.788	1	1	0	2	2.809	2.807	1	2	3
9	7.65	7.613	1	0	1	7	2.631	2.629	3	3	0
9	7.55	7.493	0	1	1	4	2.570	2.568	0	0	4
1	5.68	5.679	2	0	0	4	2.541	2.539	3	0	3
2	5.46	5.482	0	2	0	5	2.507	2.505	0	3	3
8	5.15	5.135	0	0	2			2.491	0	3	3
2	4.45	4.441	1	2	1			2.486	4	0	2
8	4.31	4.306	1	1	2	2	2.345	2.343	3	3	2
1	3.95	3.941	2	2	0	5	2.307	2.306	3	2	3
9	3.81	3.809	2	0	2	3b	2.303	2.300	3	2	3
5b	3.75	3.756	0	2	2			2.293	2	3	3
		3.739	0	2	2			2.281	2	3	3
9b	3.55	3.551	3	0	1	1b	2.220	2.218	5	0	1
1	3.48	3.473	1	3	0			2.189	4	3	1
5	3.46	3.447	0	3	1	6	2.146	2.146	0	5	1
		3.437	0	3	1			2.142	0	5	1
2b	3.28	3.277	ī	0	3	2	2.024	2.021	ī	0	5
2	3.14	3.132	2	2	2	1b	1.973	1.971	4	4	0
		3.122	2	2	2	3b	1.900	1.896	3	5	0
5	2.979	2.979	3	2	1			1.893	5	0	3
9	2.934	2.938	3	ī	2	8b	1.842	1.841	3	3	4
		2.933	3	1	2			1.834	3	3	4
2	2.891	2.887	1	3	2	1	1.829	1.827	0	6	0
2	2.874	2.873	1	3	2	1b	1.808	1.806	3	0	5

TABLE 4. Powder X-ray data for khvorovite*.

* b = broad; Debye-Scherrer RKD - 114, Fe-anode, Mn-filter, the internal standard - quartz. Analyst A.A. Agakhanov.

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$a(\mathring{A})$	11 354(2)
$u(\Lambda)$	10.960(2)
6	10.700(2) 10.271(2)
$\alpha(^{\circ})$	90.32(3)
ß	90.02(3)
þ	90.00(3)
$V(\dot{A}^3)$	1278(1)
V (A)	$\frac{1270(1)}{71}$
Space group	2
L	20.22
Absorption coefficient (mm)	20.32
F(000)	1380.8
$D_{\text{calc.}}(g/\text{cm}^{-})$	3.968
Crystal size (mm)	$0.020 \times 0.025 \times 0.030$
Radiation/monochromator	MoKa/graphite
2θ -range for structure refinement (°)	60.11
R(int) (%)	1.51
Reflections collected	7473
Independent reflections	3680
$F_{\rm o} > 4\sigma(F)$	3751
Refinement method	Full-matrix least squares on F^2 ,
	fixed weights proportional to $1/\sigma F_o^2$
No. of refined parameters	239
Final $R(obs)$ (%)	
$[F_{0} > 4\sigma(F)]$	2.89
R_1	2.96
wR ₂	5.54
Highest peak, deepest hole	1.26
$(e \dot{A}^{-3})$	-3.17
Goodness of fit on F^2	1.229

TABLE 5. Miscellaneous refinement data for khvorovite.

crystallographic information file have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from

www.minersoc.org/pages/e_journals/ dep_mat.html.

Structure description

The crystal structure of khvorovite is identical topologically to crystal structures of hyalotekite (Moore *et al.*, 1982; Christy *et al.*, 1998) and kapitsaite-(Y) (Sokolova *et al.*, 2000). The main structural unit of the structure of khvorovite is an interrupted framework of corner-shared Si, B and T tetrahedra (Fig. 5). The interstitial cations Pb²⁺ + Ba and Ca occur at the *A* and *M* sites in the channels within the framework.

In the crystal structure of khvorovite, there are four [4]-coordinated *Si* sites occupied solely by Si with $\langle Si-O \rangle = 1.617$ Å (Tables 6, 7), they give Si₈ a.p.f.u. The [4]-coordinated *B* site is occupied solely by B, with $\langle B-O \rangle = 1.478$ Å; it gives B₂ a.p.f.u. The refined site-scattering 24.70 e.p.f.u. (electrons per formula unit) for the T site (2 a.p.f.u.) indicates clearly that this site is occupied by Si and a lighter cation, i.e. boron (Table 8). The $\langle T-O \rangle = 1.605$ Å indicates that this site must be occupied by Si plus a smaller cation [cf. ^[4]B³⁺ (r = 0.11 Å) and ^[4]Si (r = 0.26 Å); Shannon (1976)] (Table 7). Hence we assign $(Si_{1,46}B_{0,54})$ to the T site; this site ideally gives (SiB) a.p.f.u. Si(1-4) tetrahedra form four-membered Si₄O₁₂ rings (Fig. 5). The T and B tetrahedra form fourmembered T₂B₂O₁₂ rings. Tetrahedra of both rings share vertices to form an interrupted [Si₈B₂T₂O₂₈] framework of ideal composition $[Si_8B_2(SiB)O_{28}]^{11-}$ p.f.u.

Each interstitial A site splits into two subsites: A(1) = A(11) + A(12) separated by 0.51(2) Å and A(2) = A(21) + A(22) separated by 0.50(2) Å (Tables 6–8). The [8]-coordinated A(11) and A(21) sites have refined site-scattering values of 116 and 106 e.p.f.u., and the eight A–O bond-

$U_{\rm eq}$	0.0155(3)	0.018(2)	0.0211(4)	0.043(3)	0.0120(3)	0.0096(4)	0.0107(9)	0.0117(6)	0.0107(6)	0.0113(3)	0.0109(3)	0.0210(17)	0.0262(19)	0.0267(19)	0.0217(16)	0.0142(14)	0.0191(15)	0.0140(13)	0.0164(14)	0.0214(9)	0.0123(6)	0.0180(7)	0.0146(6)	0.0199(16)	0.0155(15)	0.0248(9)
U^{12}	-0.0041(5)	0.003(3)	0.0035(6)	0.014(6)	-0.0009(10)	-0.0074(12)	-0.011(4)	-0.0039(9)	-0.0048(9)	-0.0041(13)	-0.0085(13)	-0.024(3)	0.007(3)	-0.020(3)	-0.002(3)	-0.001(2)	-0.010(3)	-0.010(2)	-0.005(3)	-0.011(4)	0.000(3)	-0.009(4)	-0.006(3)	-0.004(3)	-0.011(2)	-0.003(6)
U^{13}	0.0012(3)	0.0001(16)	-0.0021(5)	-0.014(4)	-0.0015(10)	0.0025(13)	0.001(4)	0.0028(10)	0.0022(9)	-0.0087(13)	0.0012(13)	-0.001(3)	-0.012(3)	0.000(3)	0.001(3)	0.007(3)	-0.004(3)	0.004(2)	0.006(3)	-0.017(4)	-0.007(4)	0.004(4)	0.000(3)	0.000(3)	0.005(3)	0.003(5)
U^{23}	-0.0016(2)	-0.0027(12)	-0.0015(3)	-0.001(3)	0.0001(3)	0.0003(4)	-0.0001(15)	0.0024(10)	-0.0030(10)	0.0012(4)	0.0002(4)	-0.007(3)	-0.010(3)	0.010(3)	0.001(3)	0.001(2)	0.003(3)	-0.001(3)	0.001(3)	-0.0008(12)	-0.0001(10)	0.0025(12)	-0.0015(11)	0.004(3)	-0.004(3)	0.0018(16)
U^{33}	0.0136(3)	0.0187(16)	0.0135(3)	0.022(3)	0.0127(4)	0.0068(6)	0.0058(17)	0.0145(12)	0.0090(11)	0.0120(6)	0.0096(5)	0.015(3)	0.029(4)	0.032(4)	0.019(4)	0.019(3)	0.008(3)	0.012(3)	0.009(3)	0.0122(16)	0.0104(13)	0.0113(14)	0.0126(14)	0.012(3)	0.017(3)	0.0082(17)
U^{22}	0.0157(5)	0.009(2)	0.0229(6)	0.049(5)	0.0103(4)	0.0108(7)	0.013(2)	0.0084(13)	0.0167(15)	0.0074(5)	0.0092(5)	0.028(4)	0.019(4)	0.028(4)	0.018(4)	0.004(3)	0.030(4)	0.018(3)	0.015(3)	0.0093(14)	0.0093(13)	0.0183(15)	0.0110(13)	0.030(5)	0.019(4)	0.040(3)
U^{11}	0.0171(5)	0.0255(3)	0.0270(6)	0.0573(5)	0.0130(4)	0.0111(7)	0.014(2)	0.0123(12)	0.0062(11)	0.0146(7)	0.0138(6)	0.019(3)	0.031(4)	0.021(4)	0.028(4)	0.019(3)	0.020(4)	0.012(3)	0.025(4)	0.043(3)	0.0171(16)	0.0244(18)	0.0202(17)	0.017(3)	0.010(3)	0.026(2)
Ν	0.00721(11)	0.0124(5)	0.00333(12)	0.0182(13)	0.22749(8)	0.0006(4)	0.0316(4)	0.2517(3)	0.2493(3)	0.26216(12)	0.28380(11)	0.3077(8)	0.2347(9)	0.2320(9)	0.3072(8)	0.1043(8)	0.1049(8)	0.0807(7)	0.0791(7)	0.0864(3)	0.1116(3)	0.1444(3)	0.1629(3)	0.3430(7)	0.3486(7)	0
у	0.1753(2)	0.2027(10)	0.17648(19)	0.2029(16)	0.00300(7)	0.5008(4)	0.3353(4)	0.5273(3)	0.5265(3)	0.32232(11)	0.72191(11)	0.6396(8)	0.4041(8)	0.4047(8)	0.6385(7)	0.5696(6)	0.5686(8)	0.4032(7)	0.4050(7)	0.2143(3)	0.6669(3)	0.7872(3)	0.2090(3)	0.5043(8)	0.5098(8)	0
x	0.1631(2)	0.1994(15)	0.8332(2)	0.799(2)	-0.0008(3)	0.31763(12)	0.4992(13)	0.1935(3)	0.8062(2)	-0.0014(4)	0.0006(3)	0.8843(7)	0.8854(8)	0.1180(8)	0.1163(7)	0.2355(7)	0.7657(7)	0.6049(6)	0.3939(7)	0.5027(10)	0.5016(10)	0.0010(10)	0.9981(9)	0.3032(7)	0.6978(6)	0
Atom	A(11)	A(12)	A(21)	A(22)	M	Г	В	Si(1)	Si(2)	Si(3)	Si(4)	0(1)	0(2)	0(3)	O(4)	0(5)	O(6)	0(7)	O(8)	(6)0	O(10)	0(11)	O(12)	0(13)	0(14)	н

 T^{ABLE} 6. Atom coordinates and anisotropic displacement parameters $({\rm \mathring{A}}^2)$ for khvorovite.

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TABLE 7. Selected interatomic distances (Å)	and angles (°) in khvorovite*.
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$ \begin{array}{c} \hline A(11) - O(11)a \\ A(11) - O(14)b \\ A(11) - O(12)c \\ A(11) - O(13)d \\ A(11) - F \\ A(11) - O(6)e \\ A(11) - O(6)e \\ A(11) - O(1)b \\ A(11) - O(3) \\ < A(11) - \phi > \end{array} $	$\begin{array}{c} 2.465(9) \\ 2.463(8) \\ 2.489(8) \\ 2.535(9) \\ 2.669(4) \\ 3.145(9) \\ 3.264(8) \\ \underline{3.44(1)} \\ \underline{2.809} \end{array}$	$\begin{array}{l} A(12)-O(14)b\\ A(12)-O(13)d\\ A(12)-O(12)c\\ A(12)-O(11)a\\ A(12)-O(6)e\\ A(12)-O(1)b\\ A(12)-F\\ A(12)-F\\ A(12)-O(8)\\ A(12)-O(3)\\ \end{array}$	2.70(1) 2.72(1) 2.76(2) 2.79(2) 2.82(1) 3.05(1) 3.17(2) 3.20(2) <u>3.28(1)</u> 2.94	$\begin{array}{l} A(21)-O(11)e\\ A(21)-O(13)f\\ A(21)-O(12)\\ A(21)-O(14)g\\ A(21)-F(1)\\ A(21)-O(5)e\\ A(21)-O(5)e\\ A(21)-O(4)f\\ A(21)-O(2)\\ \end{array}$	2.451(9) 2.521(9) 2.513(8) 2.577(8) 2.707(3) 3.101(8) 3.207(9) <u>3.486(8)</u> <u>2.815</u>
$\begin{array}{l} A(22) - O(14)g\\ A(22) - O(12)\\ A(22) - O(5)e\\ A(22) - O(13)f\\ A(22) - O(11)e\\ A(22) - O(4f)\\ A(22) - O(7)\\ A(22) - O(2)\\ A(22) - O(2)\\ A(22) - Fh\\ A(22) - O(9)\\ < A(22) - \phi > \end{array}$	2.71(1) 2.70(2) 2.83(1) 2.82(2) 2.82(3) 3.08(1) 3.18(3) 3.27(2) 3.19(3) <u>3.44(3)</u> 3.00	Short distances A(11)-A(12) A(21)-A(22)	0.51(2) 0.50(3)	$\begin{array}{l} M-F \\ M-O(12) \\ M-O(13)d \\ M-O(14)d \\ M-O(10)d \\ M-O(7)d \\ M-O(11)i \\ M-O(8)d \\ <\!\!M-\phi > \end{array}$	2.337(1) 2.357(3) 2.359(8) 2.373(8) 2.497(3) 2.512(7) 2.510(4) 2.532(8) 2.435
$\begin{array}{l} Si(1) - O(13) \\ Si(1) - O(4) \\ Si(1) - O(3) \\ Si(1) - O(5) \\ < Si(1) - O > \end{array}$	$ \begin{array}{r} 1.580(8) \\ 1.604(9) \\ 1.606(8) \\ \underline{1.656(8)} \\ 1.612 \end{array} $	Si(2)-O(14) Si(2)-O(2) Si(2)-O(6) Si(2)-O(1) <si(2)-o></si(2)-o>	$1.609(8) \\ 1.621(9) \\ 1.622(8) \\ 1.636(7) \\ 1.622$	Si(3)-O(2)c Si(3)-O(12)c Si(3)-O(9)d Si(3)-O(3) <si(3)-o></si(3)-o>	1.593(9) 1.602(3) 1.609(4) <u>1.659(8)</u> 1.616
Si(4)-O11 Si(4)-O1c Si(4)-O10j Si(4)-O4 <si(4)-o></si(4)-o>	1.604(3) 1.618(7) 1.621(3) <u>1.620(9)</u> 1.616	T-O(7)e T-O(8) T-O(6)e T-O(5) < T-O>	1.609(8) 1.585(9) 1.624(8) <u>1.600(8)</u> 1.605	B-O(9) B-O(10)e B-O(8) B-O(7) <b-o></b-o>	1.444(6) 1.471(5) 1.50(1) <u>1.50(1)</u> 1.479
$\begin{array}{l} Si(2) - O(1) - Si(4)h\\ Si(2) - O(2) - Si(3)h\\ Si(1) - O(3) - Si(3)\\ Si(1) - O(4) - Si(4)\\ Si(1) - O(5) - T\\ Si(2) - O(6) - Te \end{array}$	144.0(6) 153.8(6) 150.3(7) 145.0(6) 130.0(5) 129.8(5)			B-O(7)-Te B-O(8)-T B-O(9)-Si(3)d Be-O(10)-Si(4)j	126.0(5) 127.5(5) 127.7(3) 132.1(3)

* $\phi = O, F.$

Symmetry operators: a: -x, -y+1, -z; b: $x-\frac{1}{2}$, $y-\frac{1}{2}$, $z-\frac{1}{2}$; c: x-1, y, z; d: $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+\frac{1}{2}$; e: -x+1, -y+1, -z; f: $x+\frac{1}{2}$, $y-\frac{1}{2}$, $z-\frac{1}{2}$; g: $-x+\frac{3}{2}$, $-y+\frac{1}{2}$, $-z+\frac{1}{2}$; h: x+1, y, z; i: x, y-1, z; j: $-x+\frac{1}{2}$, $-y+\frac{3}{2}$, $-z+\frac{1}{2}$.

lengths divide into two groups: five shorter bond lengths, 2.465–2.707 Å and three longer bond lengths, 3.145–3.486 Å. Such an arrangement of anions around a central cation is characteristic of the lone-pair stereoactive behaviour of Pb²⁺ and has been reported for the Pb²⁺-dominant subsites in hyalotekite (Moore *et al.*, 1982). Hence we assign 1.44 Pb²⁺ and 1.32 Pb²⁺ a.p.f.u. to the A(11) and A(21) sites, with 72 and 66% siteoccupancies, respectively (Table 8). The [9]coordinated A(12) and [10]-coordinated A(22)sites have refined-scattering of 25 and 18 a.p.f.u., with $\langle A(12)-O \rangle = 2.94$ Å and $\langle A(22)-O \rangle = 3.00$ Å. In accord with the refined site-scattering values, we assign 0.62 Ba + 0.56 K + 0.06 Na (Table 3) to the A(12) and A(22) sites; hence these two subsites are occupied at 28 and 34%, respectively

Site	Refined site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	$\langle X - \phi^{>_{obs.}}$	Ideal composition (a.p.f.u.)
$[8]_A(11)$	116(2)	1.44 Pb + 0.56	118.08	2.809	Pb_2
$^{[9]}A(12)$	25(2)	$1.44 \square + 0.46 Ba + 0.06 Na + 0.04 K$	27.18	2.94	
$[8]_{A(21)}$	106(2)	1.32 Pb + 0.68	108.24	2.86	Pb_2
[10]A(22)	18(2)	1.32 🗆 + 0.52 K + 0.16 Ba	18.84	3.00	
$\Sigma A(11-22)$	265	1.44 Pb + 0.62 Ba + 0.56 K + 0.06 Na	272.34		Pb_4
$M_{[8]}$	42.5(2)	1.86 Ca + 0.06 Sr + 0.04 Y + 0.04 Na	41.48	2.435	Ca_2
$^{[4]}T$	24.7(2)	1.46 Si + 0.54 B	23.14	1.605	(SiB)
	L C				
$\mathbf{X} = $ cation, $\boldsymbol{\varphi}$	r = 0, F				

TABLE 8. Refined site-scattering values and assigned site-populations for khvorovite.

(Table 8). Therefore, the *A* sites are occupied by Pb^{2+} , Ba, K and minor Na; the ideal composition of the two A(1,2) sites is Pb_4^{2+} a.p.f.u. (Table 8). The interstitial [8]-coordinated *M* site is occupied mainly by Ca, with minor Sr, Y and Na, its ideal composition is Ca₂ a.p.f.u.

There are fifteen anion sites in the crystal structure of khvorovite (Table 6). The O(1-10) atoms are bridge anions for two tetrahedra of the interrupted framework and hence they are O atoms. The O(11-14) atoms are bonded to one Si atom and to three interstitial cations each, and hence they are also O atoms. The F atom is coordinated by two M (= Ca) and four A cations.

Discussion

There are three minerals with the hyalotekite-type structure: khyorovite, ideally $Pb_4^{2+}Ca_2[Si_8B_2]$ $(SiB)O_{28}]F$; hyalotekite, $(Ba,Pb^{2+},K)_4(Ca,Y)_2$ $[(B,Be)_2(Si,B)_2Si_8O_{28}]F$; and kapitsaite-(Y), (Ba,K)₄(Y,Ca)₂[Si₈B₂(B,Si)₂O₂₈]F. It seems justified to define a hyalotekite group, and this work is currently in progress (E. Grew, pers. comm., 2014). The difference between khvorovite and hyalotekite is the dominant occupancy of the A sites by Pb^{2+} and Ba, respectively. Previous chemical data for these minerals (Fig. 6, right) show a restricted variation in the Pb:Ba ratio with most of the data lying within the field of hyalotekite. However, analysis of these minerals from Darai-Pioz shows complete solid solution between khvorovite and hyalotekite from Ba-free to virtually Pb²⁺-free compositions (Fig. 6, left). Where Ba is the dominant cation, the K content of the A sites is ~0.2 a.p.f.u. Where Pb^{2+} is the dominant cation, the K content of the A sites increases linearly from ~0.2 a.p.f.u. at $Pb^{2+} + K = 2$ a.p.f.u. to ~0.9 a.p.f.u. at Pb + K = 4 a.p.f.u.

Kapitsaite-(Y) differs from hyalotekite in dominance of Y over Ca at the *M* site (Pautov *et al.*, 2000; Sokolova *et al.*, 2000). The extensive solid solution between khvorovite and hyalotekite at the Darai-Pioz locality suggests that a Pb^{2+} -analogue of kapitsaite-(Y) may be possible. From the chemical data currently available, there is no sign of any correlation between K and Y contents in these minerals.

Summary

(1) Khvorovite, ideally Pb₄²⁺Ca₂[Si₈B₂(SiB)O₂₈]
F, is a new hyalotekite-group mineral (Table 1).
(2) In the crystal structure of khvorovite, Pb²⁺ is

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FIG. 5. General view of the crystal structure of khvorovite. Si, T = (Si,B) and B tetrahedra are green, orange and red, respectively; [8]-coordinated Ca atoms at the *M* site and [8]-coordinated Pb atoms at the *A*(11) and *A*(21) sites are shown as medium pink and large yellow spheres; F atoms are shown as small blue spheres. Atoms at the *A*(12) and *A*(22) sites with <50% occupancy are not shown. The unit cell is shown by thin black lines.

dominant at the A sites and Ca is dominant at the M site.

a Pb²⁺-, Ca-analogue of kapitsaite-(Y), (Ba,K)₄(Y,Ca)₂[Si₈B₂(B,Si)₂O₂₈]F.

(3) Khvorovite is a Pb^{2+} -analogue of hyalotekite, $(Ba,Pb^{2+},K)_4(Ca,Y)_2[Si_8(B,Be)_2(Si,B)_2O_{28}]F$ and



FIG. 6. Ternary diagram of hyalotekite (Ba) – khvorovite (Pb) – "K-hyalotekite" (K). Left: ○ our data; ● our data for the grain used for structure refinement; Right: data from the literature (○ Nordenskiöld (1877); ■ Lindström (1887); □ Grew et al. (1994); × Christy et al. (1998).

Acknowledgements

The authors thank E. Grew and an anonymous reviewer for useful comments and Associate Editor S. Krivovichev for handling the manuscript. A.R. Faiziev, F.G. Gafurov, R.U. Sobirova, T.K. Berkeliyev, V.A. Muftakhov and M.A. Shodibekov are acknowledged for help during field work on the Darai-Pioz massif. V.A. Rassulov is thanked for technical support and discussions and M.A. Cooper for collection of the single-crystal X-ray data for khvorovite. AAA and OIS acknowledge financial support by the St. Petersburg State University internal grant 3.50.2099.2013 and VKG, AAA, LAP and VYK acknowledge financial support by the grant 12-05-00911-a from the Russian Foundation for Basic Research. This work was also supported by a Canada Research Chair in Crystallography and Mineralogy and by a Discovery grant from the Natural Sciences and Engineering Research Council of Canada to FCH and by Innovation Grants from the Canada Foundation for Innovation to FCH.

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