Kobyashevite, $Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$, a new devilline-group mineral from the Vishnevye Mountains, South Urals, Russia

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Abstract A new mineral kobyashevite, $Cu_5(SO_4)_2$ $(OH)_6 \cdot 4H_2O$ (IMA 2011–066), was found at the Kapital'-naya mine, Vishnevye Mountains, South Urals, Russia. It is a supergene mineral that occurs in cavities of a calcite-quartz vein with pyrite and chalcopyrite. Kobyashevite forms elongated crystals up to 0.2 mm typically curved or split and combined into thin crusts up to 1×2 mm. Kobyashevite is bluish-green to turquoise-coloured. Lustre is vitreous. Mohs hardness is 2½. Cleavage is {010} distinct. D (calc.) is 3.16 g/cm³. Kobyashevite is optically biaxial (−), α 1.602(4), β 1.666(5), γ 1.679(5), 2 V(meas.) 50(10)°. The chemical composition (wt%, electron-microprobe data) is: CuO 57.72, ZnO 0.09, FeO 0.28, SO_3 23.52, H_2O(calc.) 18.39, total 100.00. The empirical formula, calculated based on 18 O, is: $Cu_{4.96}Fe_{0.03}Zn_{0.01}S_{2.01}O_{8.04}(OH)_{5.96} \cdot 4H_2O$. Kobyashevite is triclinic, $P\overline{1}$, a 6.0731(6), b 11.0597(13), c 5.5094(6) Å, α 102.883(9)°, β 92.348(8)°, γ 92.597(9)°, V 359.87(7) Å³, $Z = 1$. Strong reflections of the X-ray powder pattern [d,Å-$I(hkl)$] are: 10.84–100(010); 5.399–40(020); 5.178–12(110); 3.590–16(030); 2.691–16(20–1, 040, 002), 2.653–12(04–1, 02–2), 2.583–12(2–11, 201, 2–1–1), 2.425–12(03–2, 211, 131). The crystal structure (single-crystal X-ray data, $R = 0.0399$) contains $[Cu_4(SO_4)_2(OH)_6]$ corrugated layers linked via isolated $[CuO_2(H_2O)_4]$ octahedra; the structural formula is $CuCu_4(SO_4)_2(OH)_6 \cdot 4H_2O$. Kobyashevite is a devilline-group member. It is named in memory of the Russian mineralogist Yuriy Stepanovich Kobyashev (1935–2009), a specialist on mineralogy of the Urals.

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Introduction

Seven copper sulfate minerals with both OH groups and H_2O molecules and without other species-defining cations or anions were known before: langite, $Cu_4(SO_4)$ $(OH)_6 \cdot 2H_2O$, montetrisaite, $Cu_6(SO_4)(OH)_{10} \cdot 2H_2O$, posnjakite, $Cu_4(SO_4)(OH)_6 \cdot H_2O$, ramsbeckite, Cu_{15} $(SO_4)_4(OH)_{22} \cdot 6H_2O$, redgillite, $Cu_6(SO_4)(OH)_{10} \cdot H_2O$, schulenbergite, $Cu_7(SO_4)_2(OH)_{10} \cdot 3H_2O$, and wroewolfeite, $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$. These minerals, showing significant structural diversity, have the same origin: they are formed as products of supergene alteration (oxidation) of copper sulfides.

The present paper describes another mineral belonging to this chemical family and having the same genesis. It was named **kobyashevite** (Cyrillic: кобяшевит) in memory of the Russian mineralogist Yuriy Stepanovich Kobyashev

(1935–2009) who worked in the Ilmeny Natural Reserve, Miass, Chelyabinsk Oblast, Russia. He was a well-known specialist on the mineralogy of the Urals (Kobyashev and Nikandrov 2007) and, in particular, of the Vishnevye Mountains (Kobyashev et al. 1998).

Kobyashevite is a member of the devilline group and the natural analogue of the synthetic compound $Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$ (Table 1), also known as a product of atmospheric corrosion of copper and bronze objects[1] (Strandberg et al. 1995).

The new mineral and its name have been approved by the IMA CNMNC, No. 2011–066. The type specimen of kobyashevite is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, the registration number is 4152/1.

Occurrence and general appearance

The type locality of kobyashevite is the Kapital'naya mine, Vishnevye Mountains, Chelyabinsk Oblast, South Urals, Russia. This underground mine, operated for Nb and Ta (pyrochlore ore), was abandoned and flooded in mid-1990s. The specimens of the mineral were collected in early 1990s by local miner and amateur mineralogist Georgiy E. Antonov.

Kobyashevite was found in small cavities of a calcite-quartz vein with minor amounts of pyrite and chalcopyrite. This vein cross-cuts fenites of the Vishnevogorsky alkaline complex (Kobyashev et al. 1998). The new mineral occurs as elongated crystals up to 0.1 mm, rarely 0.2 mm in size. They show a prismatic habit but, in fact, are shaped by faces of three or more pinacoids (Fig. 1a). The crystals are typically curved or split, divergent (Fig. 1b, c) and combined in groups (Fig. 1c, d) on the surface of calcite or quartz. Thin, open-work crystal crusts of kobyashevite are up to 1×2 mm in size.

Physical properties and optical data

Kobyashevite is transparent, bluish-green to turquoise-coloured, with pale bluish green streak. The lustre is vitreous. The mineral does not fluoresce in UV nor in cathode rays. Its Mohs hardness is 2½. Kobyashevite is brittle. The cleavage is {010} distinct, the fracture is stepped. Density could not be measured because of small grain size and the open-work character of aggregates; the calculated density is 3.155 gcm^{-3}.

Kobyashevite is optically biaxial (−), α=1.602(4), β=1.666(5), γ=1.679(5), 2 V (meas.) = 50(10)°, 2 V (calc.) = 47°. Dispersion of optical axes is strong, $r < v$. Orientation: Z is close to the crystal elongation direction. Pleochroism is

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Table 1 Comparative data for kobyashevite and its synthetic analogue

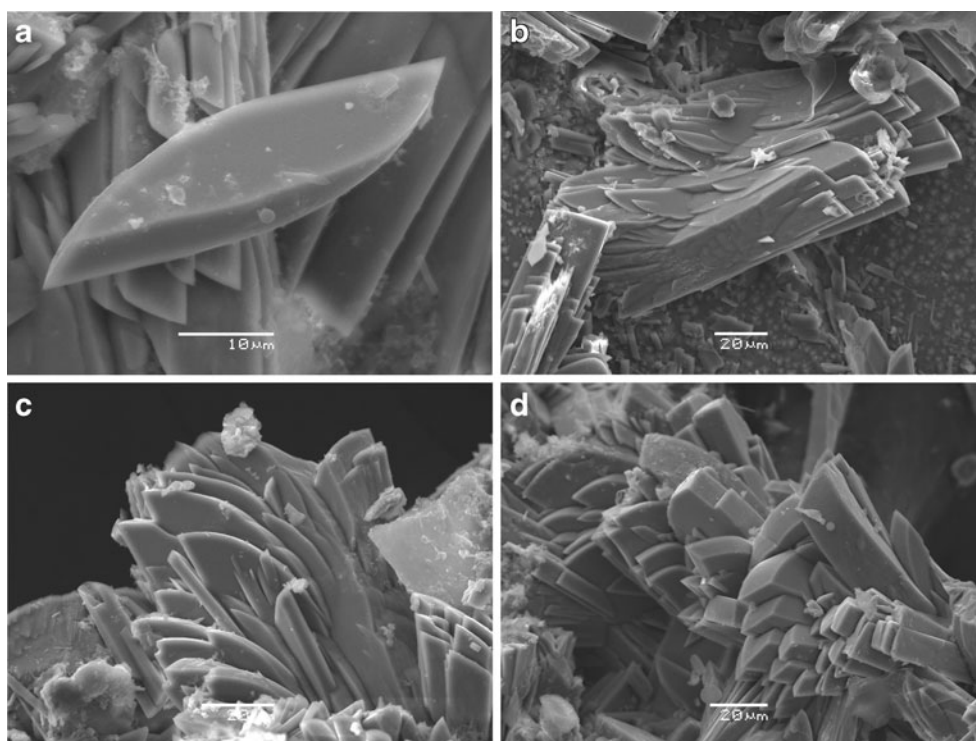| Mineral/compound	Kobyashevite	Synthetic
Formula	$Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$	$Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.0731(6)	6.064(2)
b, Å	11.0597(13)	11.012(6)
c, Å	5.5094(6)	5.490(2)
α, °	102.883(9)	102.68(4)
β, °	92.348(8)	92.43(3)
γ, °	92.597(9)	92.06(3)
V, Å^3	359.87(7)	357.0(5)
Z	1	1
Strong lines	10.84–100	10.81–100
Of the X-ray powder-	5.40–40	5.39–47
Diffraction	5.18–12	5.16–17
Pattern:	3.590–16	3.591–22
d, Å–I, %	2.691–16	2.698–28
	2.653–12	2.579–26
	2.583–12	2.424–31
	2.425–12	2.352–20
Strong bands of the IR	3588	3589
Absorption	3546	3549
spectrum, cm^{-1}	3049 (broad)	3054 (broad)
	1090	1092
	785	783
	669	668
	616	618
	495	495
Density (calc.), g cm^{-3}	3.16	3.18
References	this work	Strandberg et al. 1995

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medium, $Z > Y > X$; the mineral is bluish-green in all sections but the intensity depends on orientation.

Chemical composition

Chemical data of kobyashevite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with the INCA-Energy 350 energy-dispersive spectrometer. An operating voltage was 20 kV, a beam current was 1 nA, the electron beam diameter was 5 μm. The following standards were used: $CuFeS_2$ (Cu, Fe) and ZnS (Zn, S).

The average of 4 analyses chemical composition of kobyashevite (wt%, ranges are in parentheses) is: CuO 57.72 (56.7–58.4), ZnO 0.09 (0.0–0.2), FeO 0.28 (0.2–0.4), SO_3 23.52 (22.2–24.7), H_2O (calc.) 18.39, total 100.00. The H_2O content was assigned by difference; the correctness of the value is clearly confirmed by the crystal

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[1] In some papers the name "strandbergite" is used for this compound formed in the result of corrosion of artificial metallic objects containing copper (He 2002).

Fig. 1 Morphology of kobyashevite crystals and aggregates, SEM (SE) images

structure refinement. Contents of other elements with atomic numbers higher than 8 are below detection limits.

The empirical formula, calculated on the basis of 18 O *apfu*, is: $Cu_{4.96}Fe_{0.03}Zn_{0.01}S_{2.01}O_{8.04}(OH)_{5.96} \cdot 4H_2O$. The simplified formula is $Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$, which requires CuO 58.15, SO_3 23.41, H_2O 18.44, total 100.00 wt.%.

The Gladstone-Dale compatibility index $[1-(K_p/K_c)]$ (Mandarino 1981) value is −0.014 (*superior*).

X-ray crystallography and crystal structure

X-ray powder-diffraction data for kobyashevite (Table 2) were obtained with a STOE IPDS II single-crystal diffractometer equipped with an image plate detector ($MoK\alpha$ radiation; the distance between sample and detector 200 mm) using the Gandolfi method. The X-ray powder patterns of kobyashevite and synthetic $Cu_5(SO_4)_2$ $(OH)_6 \cdot 4H_2O$ (Strandberg et al. 1995) are very close (Table 1). The unit cell parameters of kobyashevite calculated from the powder data are: $a=6.08(4)$, $b=11.07(8)$, $c=5.51$ (4)Å, $\alpha=102.8(2)°$, $\beta=92.4(2)°$, $\gamma=92.5(2)°$, $V=360(2)Å^3$.

Single-crystal X-ray studies of kobyashevite were carried out using an Oxford Xcalibur S diffractometer equipped with a CCD detector. The structure was solved by direct methods and refined with the use of SHELX software package (Sheldrick 2008) to $R=0.0399$ for 1,218 unique reflections with $I>2\sigma(I)$. Absorption correction was applied according to the shape of the crystal. Crystal data, data collection information and structure refinement details are

given in Table 3, atom coordinates and equivalent isotropic displacement parameters in Table 4, anisotropic displacement parameters for all atoms except hydrogen in Table 5, and selected interatomic distances in Table 6. All hydrogen atoms were found during the refinement and their positions were softly constrained by setting the O–H distances equal to 0.90 Å. The data on H–bonds are presented in Table 7. Bond-valence sums are reported in Table 8. We have preferred direct methods for the solution of the kobyashevite structure, in spite of the existence of the structure model for its synthetic analogue (Strandberg et al. 1995), because of wide diversity of related compounds demonstrating differences in fine structure details (see Discussion).

As our data show, in the structural aspect kobyashevite and its synthetic analogue studied by Strandberg et al. (1995) are almost identical. The structure of kobyasheite (Fig. 2a) contains $[Cu_4(SO_4)_2(OH)_6]$ corrugated layers (Table 9) coplanar to *ac*. The constitution of each layer is a cationic sheet formed by edge-connected Cu(1)−, Cu(2)− and Cu(3)-centered octahedra (Fig. 2b). Isolated octahedra $[Cu(4)O_2(H_2O)_4]$ link these layers. Two vertices [O(6)] of each Cu(4)-centered octahedron are shared with SO_4 tetrahedra, while the other four vertices [O(8) and O(9)] are O atoms of H_2O molecules. Cu(4)-centered octahedra show very strong Jahn-Teller distortion and could be considered as elongated tetragonal dipyramids: two Cu(4)–O(6) distances are significantly longer than Cu(4)–O(8) and Cu(4)–O(9) distances (Table 6). Thus, the interlayer content in kobyashevite can be considered as Cu $(H_2O)_4$ (Table 9). However it is worthy to note that the

Table 2 X-ray powder diffraction data for kobyashevite

I_{obs}	d_{obs}, Å	I_{calc}[a]	d_{calc}[b], Å	$h\,k\,l$
100	10.84	100	10.764	010
40	5.399	43	5.382	020
12	5.178	12	5.158	110
8	4.421	9	4.420	011
8	4.130	2, 6	4.140, 4.125	1–20, 10–1
8	3.936	3, 6	3.942, 3.917	1–11, 120
16	3.590	18	3.588	030
8	3.358	8	3.352	03–1
4	3.174	5	3.166	1–30
1	3.067	1	3.079	1–2–1
3	2.961	2, 1	2.959, 2.957	2–10, 1–31
3	2.910	3	2.901	121
4	2.761	5	2.752	01–2
16	2.691	9, 8, 2	2.699, 2.691, 2.682	20–1, 040, 002
12	2.653	1, 13	2.657, 2.650	04–1, 02–2
12	2.583	2, 8, 6	2.603, 2.580, 2.580	2–11, 201, 2–1–1
6	2.474	2, 5, 1, 1	2.483, 2.476, 2.475, 2.469	2–21, 22–1, 012, 1–12
12	2.425	6, 8, 1	2.426, 2.425, 2.415	03–2, 211, 131
8	2.355	11	2.353	2–2–1
2	2.259	1	2.260	13–2
9	2.204	5, 7	2.210, 2.197	022, 221
7	2.160	10	2.158	04–2
4	2.093	5	2.094	2–3–1
5	2.029	6	2.027	2–41
4	1.959	1, 3	1.958, 1.955	202, 231
2	1.899	3	1.901	05–2
3	1.850	4	1.848	2–4–1
3	1.797	3	1.794	060
4	1.733	2, 6	1.738, 1.732	25–1, 241
1	1.685	1	1.691	103
1	1.673	3	1.676	06–2
1	1.632	2	1.633	2–5–1
3	1.588	3	1.587	22–3
5	1.539	3, 4, 1	1.540, 1.539, 1.538	26–1, 2–23, 2–13
4	1.513	3, 2	1.515, 1.512	400, 4–10
2	1.478	3, 2	1.480, 1.473	4–20, 24–3

[a] Only reflections with $I_{calc} \geq 1$ are given; [b] Calculated for unit cell parameters obtained from single-crystal data

Table 3 Crystal data, data collection information and structure refinement details for kobyashevite

Formula	$Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$
Space group	$P\bar{1}$
Unit cell parameters (Å/°)	a=6.0731(6) α=102.883(9)
	b=11.0597(13) β=92.348(8)
	c=5.5094(6) γ=92.597(9)
V (Å^3), Z	359.87(7), 1
$F(000)$	335
Density (calculated) (g/cm^3)	3.16
μ (mm^{-1})	7.7
Crystal dimensions (mm^3)	$0.04 \times 0.07 \times 0.16$
Diffractometer	Oxford Xcalibur S CCD
Temperature (K)	293(2)
Radiation	Mo$K\alpha$, λ=0.71073 Å
θ range (°)	3.36–32.58
h,k,l ranges	$-9 \leq h \leq 9, -16 \leq k \leq 16, -8 \leq l \leq 8$
Total reflections measured	11,616
Unique reflections	2,468 (R_{int}=0.0844)
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
$R1$ for $I>2\sigma(I)$	0.0399
$wR2$	0.0656
Reflections used [$I>2\sigma(I)$]	1,218
Number of parameters refined	144
$\Delta\rho_{min}, \Delta\rho_{max}$ (e/Å^3)	−0.689, 0.581
GooF	0.815

(Bruker Optics) at the resolution of 4 cm^{-1} and the number of scans of 16. A pellet of pure KBr was used as a reference.

The IR spectrum of kobyashevite (Fig. 3) is different from those of other natural copper sulfates but is almost identical to the spectrum of its synthetic analogue (Table 1). Absorption bands in the IR spectrum of kobyashevite and their assignments are (cm^{-1}; s—strong band, w—weak band, sh—shoulder): 3588, 3546, 3480w, 3455w (O–H stretching, weak hydrogen bonds), 3230, 3049 s, 2945, 2540w (O–H stretching, strong hydrogen bonds), 1630 (H–O–H bending), 1090s (asymmetric S–O stretching, degenerate mode), 989w (symmetric S–O stretching, non-degenerate mode), 945w, 785 s, 750sh (Cu···O–H bending), 669, 616 s (O–S–O bending), 512, 495, 458w, 436w, 419w (Cu···O stretching). Diffuse absorption in the range 500–800 cm^{-1} can be due to libration modes of H_2O molecules. Low intensity of the band of symmetric S–O stretching vibrations reflects relatively small distortion of SO_4 tetrahedra.

The wavenumbers of O–H stretching vibrations estimated from D-A distances (Table 6) using the correlation by Libowitzky (1999) are 3582, 3571, 3564 and 3461 cm^{-1} for OH groups and 3471, 3370, 3002 and 2604 for H_2O molecules. The number of O–H-stretching bands observed in the IR spectrum (8) coincides with the

structure of kobyashevite can be considered as a combination of brucite-like octahedral layers linked by trimers formed by 1 Cu-centered octahedron and 2 SO_4 tetrahedra.

Infrared spectroscopy

Kobyashevite powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer

Table 4 Atom coordinates and isotropic displacement parameters ($Å^2$) for kobyashevite

Atom	x/a	y/b	z/c	U_{eq}
Cu(1)	0	0	0	0.0147(2)
Cu(2)	0.5	0	0	0.0153(2)
Cu(3)	0.75095(9)	−0.00256(6)	0.50483(11)	0.01379(14)
Cu(4)	0.5	0.5	0	0.0306(3)
S	0.82222(18)	0.27673(12)	0.2863(2)	0.0178(3)
O(1)	0.7350(5)	−0.0911(3)	0.8362(6)	0.0148(7)
H(1)	0.713(7)	−0.1710(14)	0.838(8)	0.014(7)[a,b]
O(2)	0.5030(5)	0.0829(3)	0.7097(6)	0.0150(8)
H(2)	0.512(7)	0.1660(10)	0.744(8)	0.014(7)[a,b]
O(3)	0.0089(5)	0.0791(3)	0.7108(5)	0.0133(7)
H(3)	−0.009(7)	0.1599(12)	0.758(8)	0.014(7)[a,b]
O(4)	0.7673(4)	0.1421(3)	0.2472(5)	0.0168(7)
O(5)	0.9675(5)	0.2970(3)	0.0928(6)	0.0277(8)
O(6)	0.6184(5)	0.3422(4)	0.2754(6)	0.0313(9)
O(7)	0.9387(5)	0.3213(3)	0.5325(6)	0.0274(9)
O(8)	0.2281(6)	0.4931(4)	0.1509(7)	0.0350(10)
H(81)	0.139(6)	0.424(2)	0.122(9)	0.026(15)[a]
H(82)	0.165(9)	0.555(4)	0.252(9)	0.09(3)[a]
O(9)	0.3910(5)	0.3624(4)	0.7086(7)	0.0248(9)
H(91)	0.249(3)	0.365(6)	0.663(9)	0.052(19)[a]
H(92)	0.488(8)	0.390(6)	0.613(10)	0.09(3)[a]

[a] U_{iso};

[b] constrained to a common value during refinement

Table 6 Selected interatomic distances (Å) in kobyashevite

Cu(1)–O(1) 1.936(3) × 2	Cu(3)–O(2) 1.955(3)
−O(3) 1.983(3) × 2	−O(3) 1.956(3)
−O(4) 2.393(3) × 2	−O(3) 2.015(3)
	−O(2) 2.056(3)
Cu(2)–O(1) 1.923(3) × 2	−O(1) 2.259(3)
−O(2) 2.014(3) × 2	−O(4) 2.365(3)
−O(4) 2.365(3) × 2	
	Cu(4)–O(8) 1.885(3) × 2
S–O(5) 1.460(3)	−O(9) 2.016(4) × 2
−O(6) 1.468(3)	−O(6) 2.659(3) × 2
−O(4) 1.474(4)	
−O(7) 1.477(3)	

describe bands above 3592 cm^{-1}. However based on this correlation we can suppose that the bands in the ranges of 2540–3230 and 3455–3588 cm^{-1} observed in the IR spectrum of kobyashevite correspond to H_2O molecules and OH groups, respectively. The band at 2540 cm^{-1} can be definitely assigned to the hydrogen bond O(8)–H(81) ···O (5) with the angle *D*-H···*A* of 178° (Table 7) formed by strongly polarized H(81)H(82)O(8) molecule.

Discussion

Kobyashevite is a devilline-group mineral. Other members of this group and some related minerals (generally, more than ten mineral species) show a structural similarity with kobyashevite (Table 9; Figs. 4, 5). Niedermayrite, $CdCu_4$ $(SO_4)_2(OH)_6 \cdot 4H_2O$, campigliaite, $MnCu_4(SO_4)_2$ $(OH)_6 \cdot 4H_2O$, ktenasite, $Zn(Cu,Zn)_4(SO_4)_2(OH)_6 \cdot 6H_2O$, aldridgeite $(Cd,Ca)(Cu,Zn)_4(SO_4)_2(OH)_6 \cdot 3H_2O$, and

number of different hydrogen bonds. There are essential discrepancies between estimated and observed wavenumbers in the range 3200–3500 cm^{-1}. Note that in the correlation by Libowitzky (1999) the value of the *D*-H···*A* angle and the nature of cations coordinating the *D* atom are not taken into account. In addition, it does not

Table 5 Anisotropic displacement parameters ($Å^2$) for kobyashevite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0.0104(4)	0.0232(6)	0.0105(4)	0.0039(4)	0.0013(3)	−0.0008(4)
Cu(2)	0.0103(4)	0.0235(6)	0.0125(4)	0.0044(4)	0.0033(3)	0.0013(4)
Cu(3)	0.0083(2)	0.0217(4)	0.0111(3)	0.0031(2)	0.0018(2)	0.0000(2)
Cu(4)	0.0229(5)	0.0261(6)	0.0355(6)	−0.0090(5)	0.0141(4)	−0.0078(4)
S	0.0181(6)	0.0150(7)	0.0197(6)	0.0019(5)	0.0051(5)	0.0012(5)
O(1)	0.0137(15)	0.016(2)	0.0152(17)	0.0051(15)	0.0005(13)	−0.0001(15)
O(2)	0.0143(16)	0.018(2)	0.0133(17)	0.0040(16)	−0.0001(13)	−0.0004(16)
O(3)	0.0102(15)	0.015(2)	0.0134(17)	0.0004(15)	0.0017(13)	0.0006(15)
O(4)	0.0152(15)	0.015(2)	0.0210(18)	0.0049(15)	0.0028(13)	0.0008(15)
O(5)	0.0334(19)	0.023(2)	0.0260(19)	0.0030(16)	0.0188(16)	−0.0046(17)
O(6)	0.0285(19)	0.029(3)	0.039(2)	0.0101(19)	0.0093(16)	0.0134(18)
O(7)	0.0253(18)	0.030(2)	0.0217(18)	−0.0064(16)	0.0011(15)	0.0039(17)
O(8)	0.027(2)	0.020(2)	0.051(3)	−0.007(2)	0.0217(18)	−0.0081(18)
O(9)	0.0149(18)	0.029(2)	0.028(2)	0.0010(17)	0.0075(16)	−0.0029(17)

Table 7 Hydrogen bonds in kobyashevite (*D*—donor, *A*—acceptor)

D-H	d(*D*-H), Å	*D*-H···*A*	d(*D*-*A*), Å	∠(*D*-H···*A*)°	H-*D*-H	∠(H-*D*-H)°
O(1)–H(1)	0.890(10)	O(1)–H(1)…O(5)*a*	3.052(5)	120(3)		
O(2)–H(2)	0.894(10)	O(2)–H(2)…O(9)	3.196(5)	154(4)		
O(3)–H(3)	0.887(10)	O(3)–H(3)…O(5)*b*	2.853(5)	139(4)		
		O(3)–H(3)…O(7)*c*	3.093(5)	133(3)		
O(8)–H(81)	0.901(10)	O(8)–H(81)…O(5)*c*	2.578(5)	175(5)	H(81)–O(8)–H(82)	110(5)
O(8)–H(82)	0.894(10)	O(8)–H(82)…O(7)*d*	2.649(5)	175(6)		
O(9)–H(91)	0.892(10)	O(9)–H(91)…O(7)*c*	2.858(4)	164(6)	H(91)–O(9)–H(92)	115(5)
O(9)–H(92)	0.895(10)	O(9)–H(92)…O(6)	2.777(4)	141(6)		

a −x+2, −y, −z+1; *b* x−1, y, z+1; *c* x−1, y, z; *d* −x+1, −y+1, −z+1

O–H distances are in the ranges of standard values for X-ray diffraction experiment

Table 8 Bond order calculations for kobyashevite. Parameters taken from Brese and O'Keeffe (1991) and Ferraris and Ivaldi (1988)

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	S	Σ	H–bonds contribution	Σ_{total}
O(1)	0.50 $^{×2↓}$	0.52 $^{×2↓}$	0.21			1.23	−0.12(O(5))	1.11
O(2)		0.40 $^{×2↓}$	0.47 0.36			1.23	−0.10(O(9))	1.13
O(3)	0.44 $^{×2↓}$		0.47 0.40			1.31	−0.17(O(5))−0.11(O(7))	1.03
O(4)	0.14 $^{×2↓}$	0.16 $^{×2↓}$	0.16		1.50	1.96		1.96
O(5)					1.56	1.56	+0.12(O(1)) +0.17(O(3)) +0.30(O(8))	2.15
O(6)				0.07 $^{×2↓}$	1.52	1.59	+0.19(O(9))	1.78
O(7)					1.49	1.49	+0.11(O(3)) +0.25(O(8)) +0.16(O(9))	2.01
O(8)				0.57 $^{×2↓}$		0.57	−0.30(O(5))−0.25(O(7))	0.02
O(9)				0.40 $^{×2↓}$		0.40	+0.10(O(2))−0.16(O(7))−0.19(O(6))	0.15
Σ	2.16	2.16	2.07	2.08	6.07			

Fig. 2 Crystal structure of kobyashevite: **a** general view isolated coordination figures around the Cu(4) atoms [CuO₂(H₂O)₄] linking [Cu₂(OH)₃SO₄] layers are well visible and the unit cell is shown (H atoms are small black circles); **b** cationic sheet formed by the edge-connected coordination polyhedra around the atoms Cu(1), Cu(2) and Cu(3)
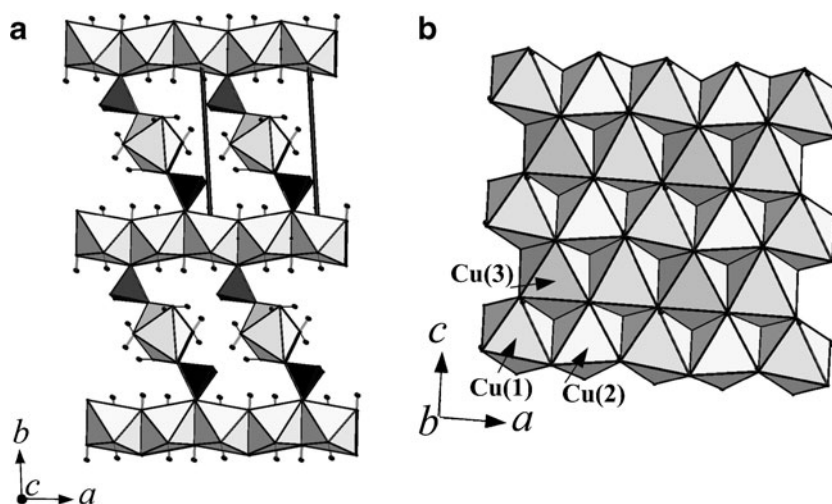
Table 9 Comparative crystal data for kobyashevite and structurally related sulfate minerals

Mineral	Formula	Crystal system, sp. gr., Z	Unit cell parameters a / α	b / β	c(Å) / γ(°)	V, Å³	Composition of layer	Interlayer content	References
Kobyashevite	$Cu_5(SO_4)_2(OH)_6 \cdot 4H_2O$	Triclinic, $P\bar{1}$, 1	6.073(6) 102.88(9)	11.060(13) 92.35(8)	5.509(6) 92.60(9)	359.87(7)	$Cu_4(SO_4)_2(OH)_6$	$Cu(H_2O)_4$	this work
Niedermayrite	$CdCu_4(SO_4)_2(OH)_6 \cdot 4H_2O$	Monoclinic, $P2_1/m$, 2	5.543(1)	21.995(4) 92.04(3)	6.079(1)	740.7(2)	$Cu_4(SO_4)_2(OH)_6$	$Cd(H_2O)_4$	Giester et al. 1998
Campigliaite	$MnCu_4(SO_4)_2(OH)_6 \cdot 4H_2O$	Monoclinic, $C2$, 4	21.725(8)	6.118(6) 100.40(5)	11.233(7)	1468.5(18)	$Cu_4(SO_4)_2(OH)_6$	$Mn(H_2O)_3$	Sabelli 1982
Ktenasite	$Zn(Cu,Zn)_4(SO_4)_2 (OH)_6 \cdot 6H_2O$	Monoclinic, $P2_1/c$, 2	5.589(1)	6.166(1) 95.55(1)	23.751(7)	814.7(3)	$(Cu,Zn)_4(SO_4)_2(OH)_6$	$Zn(H_2O)_6$	Mellini and Merlino 1978
Serpierite	$Ca(Cu,Zn)_4(SO_4)_2 (OH)_6 \cdot 3H_2O$	Monoclinic, $C2/c$, 8	22.186(2)	6.250(2) 113.36(1)	21.853(2)	2781.8(10)	$(Cu,Zn)_4(SO_4)_2(OH)_6$	$Ca(H_2O)_3$	Sabelli and Zanazzi 1968
Aldridgeite	$(Cd,Ca)(Cu,Zn)_4 (SO_4)_2(OH)_6 \cdot 3H_2O$	Monoclinic, $C2/c$, 8	22.049(2)	6.212(2) 113.19(3)	21.839(2)	2749.6(10)	$(Cu,Zn)_4(SO_4)_2(OH)_6$	(Cd, Ca)(H₂O)₃	Elliott and Pring 2010
Devilline	$CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$	Monoclinic, $P2_1/c$, 8	20.870(2)	6.135(2) 102.44(1)	22.191(3)	2774.6(10)	$Cu_4(SO_4)_2(OH)_6$	$Ca(H_2O)_3$	Sabelli and Zanazzi 1972
Lautenthalite	$PbCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$	Monoclinic, $P2_1/c$, 8	21.642(8)	6.040(2) 108.2(1)	22.544(8)	2799.5(17)	$Cu_4(SO_4)_2(OH)_6$ [a]	$Pb(H_2O)_3$ [a]	Medenbach and Gebert 1993
Orthoserpierite	$CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$	Orthorhombic, $Pca2_1$, 8	22.10(2)	6.20(2)	20.39(2)	2,794(10)	$Cu_4(SO_4)_2(OH)_6$ [b]	$Ca(H_2O)_3$ [b]	Krause and Täuber 1992
Christelite	$Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4H_2O$	Triclinic, $P\bar{1}$, 1	5.4143(8) 94.32(3)	6.336(1) 90.06(2)	10.470(3) 90.27(2)	358.15(13)	$Cu_2Zn_2(SO_4)_2(OH)_6$	$Zn(H_2O)_4$	Adiwidjaja et al. 1996
Wroewolfeite	$Cu_4(SO_4)(OH)_6 \cdot 2H_2O$	Monoclinic, Pc, 2	6.045(1)	5.646(1) 93.39(1)	14.337(2)	488.5(1)	$Cu_4(SO_4)(OH)_6(H_2O)$	H_2O	Hawthorne and Groat 1985
Langite	$Cu_4(SO_4)(OH)_6 \cdot 2H_2O$	Monoclinic, Pc, 2	7.137(3)	6.031(5) 90.00(1)	11.217(1)	482.8(5)	$Cu_4(SO_4)(OH)_6(H_2O)$	H_2O	Gentsch and Weber 1984
Posnjakite	$Cu_4(SO_4)(OH)_6 \cdot H_2O$	Monoclinic, Pa, 2	10.578(5)	6.345(3) 117.98(5)	7.863(3)	466.1(4)	$Cu_4(SO_4)(OH)_6(H_2O)$	absent	Mellini and Merlino 1979

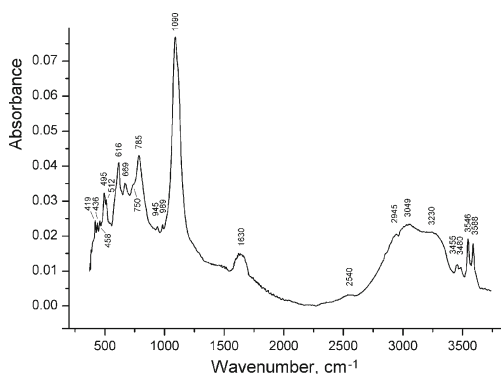[a] by analogy with its Ca-dominant analogue devilline; [b] by analogy with its monoclinic analogue serpierite

Fig. 3 IR spectrum of kobyashevite

dimorphous serpierite and devilline, $CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$, contain the same $[Cu_4(SO_4)_2(OH)_6]$ corrugated layers and differ from kobyashevite only in the type of cation occupying the interlayer site [the Cu(4) site] and, in some cases, in the number of H_2O molecules in the interlayer space. The list of related natural sulfates can be extended to lautenthalite, $PbCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$, and orthoserpierite, $CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$, as well as to christelite, $Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4H_2O$, a mineral showing Cu,Zn-ordering in the corrugated layer $(Cu_2Zn_2(SO_4)_2 (OH)_6)$ (for references see Table 9). According to

Pushcharovsky et al. (1998), the structural formula of this layer in kobyashevite and related copper sulfates can be presented as: $^2_\infty[Cu^\circ_4 S^t_2 O_8(OH)_6]$.

For clear comparison with all these minerals, the idealized structural formula of kobyashevite can be written as $CuCu_4(SO_4)_2(OH)_6 \cdot 4H_2O$ [or $^iCu^lCu_4(SO_4)_2(OH)_6 \cdot 4H_2O$ where ^iCu occupies the interlayer site Cu(4) while ^lCu atoms are located in $Cu_4(SO_4)_2(OH)_6$ layers, in the Cu(1), Cu(2) and Cu(3) sites]. All these minerals have the same ratios Me: SO_4:(OH) = 5:2:6.

The linear trimers formed by 1 Me octahedron and 2 SO_4 tetrahedra, like those in kobyashevite, are typical for numerous sulfates, e.g. blödite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$, in which Me=Mg (Pushcharovsky et al. 1998).

Some natural copper sulfates without an interlayer cation site are also structurally related to the above mentioned minerals. Those are posnjakite, $Cu_4(SO_4)(OH)_6 \cdot H_2O$, and dimorphous wroewolfeite and langite, $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$. They contain the layer $[Cu_4(SO_4)(OH)_6(H_2O)]$ instead of $[Cu_4(SO_4)_2(OH)_6]$ (Table 9). In the structures of wroewolfeite, langite and posnjakite, SO_4 tetrahedra are attached to one side of the sheet formed by Cu-centered octahedra (Hawthorne and Groat 1985), rather than both sides as in the structures of serpierite, devilline, ktenasite, campigliaite, christelite, niedermayrite and kobyashevite.
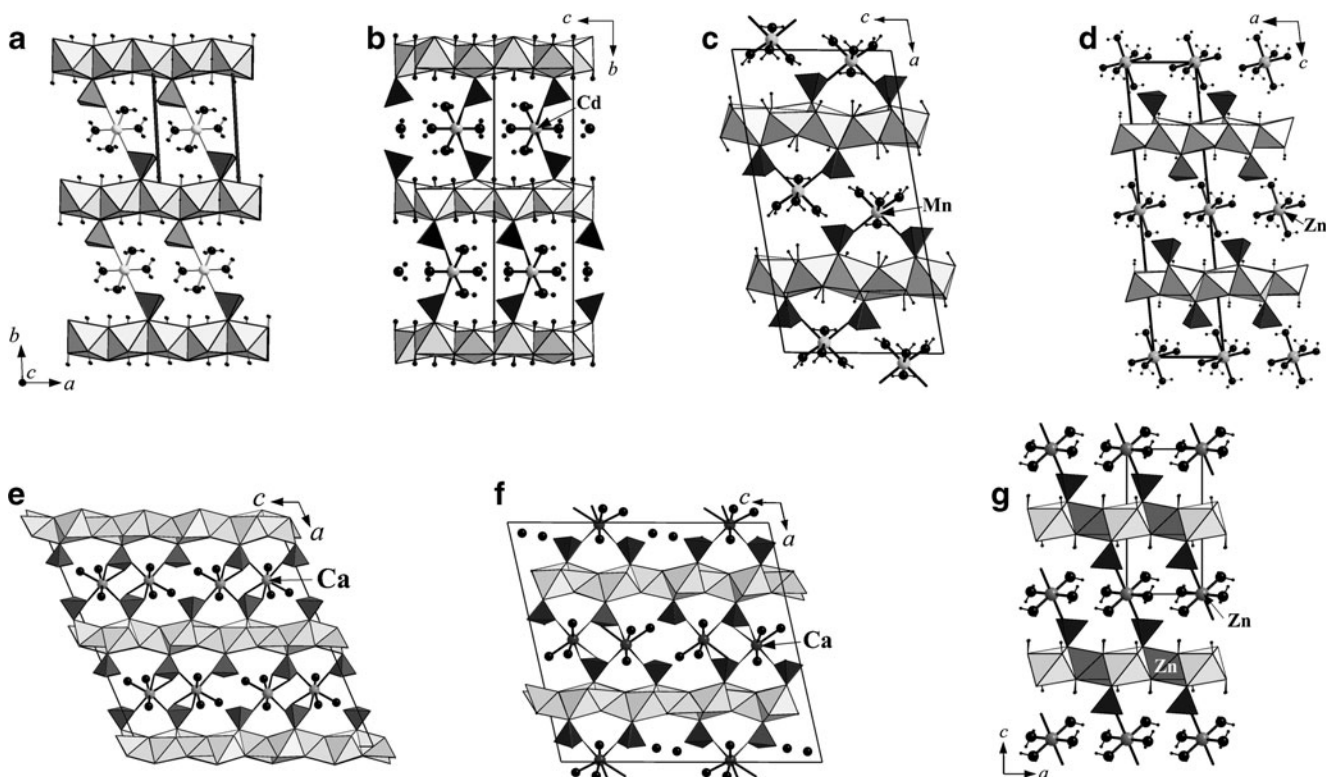

Fig. 4 Crystal structures of kobyashevite (**a**), niedermayrite (**b**), campigliate (**c**), ktenasite (**d**), serpierite (**e**), devilline (**f**), and christelite (**g**). Cu-centered polyhedra [(Cu,Zn) in **d** and **e** and (Zn,Cu) in **g**] are light-grey, SO_4 tetrahedra are black. *Large black circles* mark the positions of O atoms of H_2O molecules, *small black circles* are H atoms. For references see Table 9
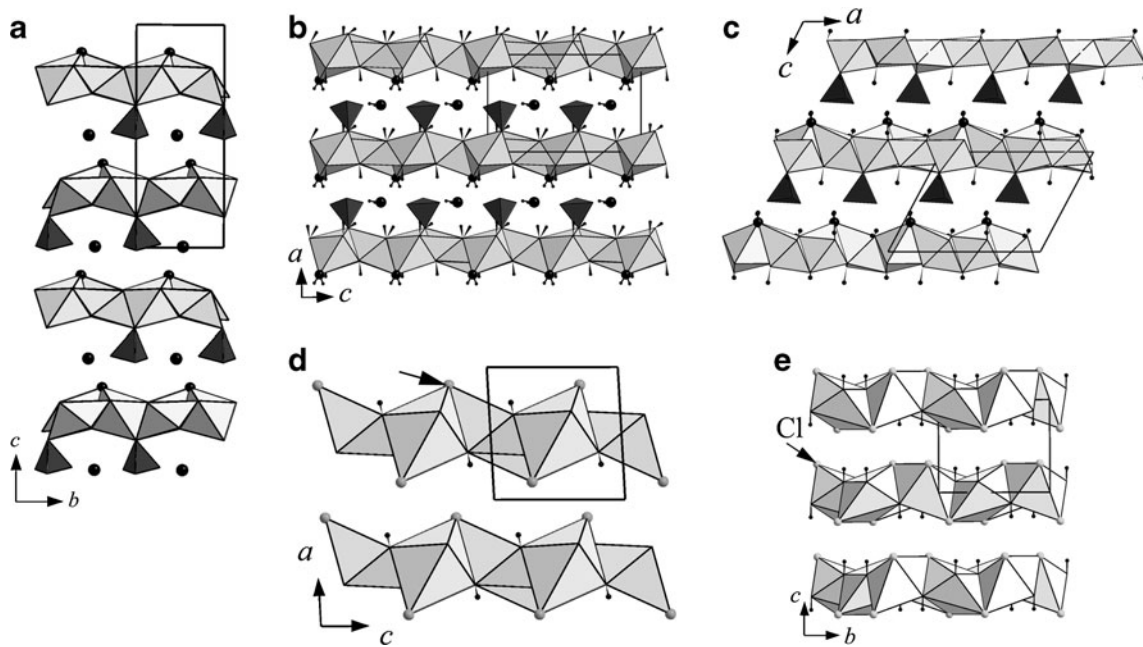
Fig. 5 Crystal structures of wroewolfeite (**a**), langite (**b**), posnjakite (**c**), botallackite (**d**), and belloite (**e**). Legend is the same as in Fig. 4. For references see text and Table 9

Similar sheets consisting of Cu polyhedra were described in chloro-hydroxide minerals belloite, Cu(OH)Cl (Effenberger 1984; Schlüter et al. 2000), and botallackite, $Cu_2(OH)_3Cl$ (Hawthorne 1985). Tetrahedral anions are absent in their structures and adjacent Cu layers are bonded with H–bonds.

All above-listed minerals contain complex layers with the general formula written by Hawthorne and Groat (1985) as $[M_4X_n\varphi_{8-n}]$ in which M = octahedrally coordinated cations, X = tetrahedral anions SO_4^{2-} and φ = O, OH, H_2O. In this formula, $n=2$ for kobyashevite and other minerals with SO_4 tetrahedra attached to both sides of the cationic (M) sheet (Fig. 4), $n=1$ for wroewolfeite, langite, and posnjakite and $n=0$ for belloite and botallackite (Fig. 5).

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