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THE CRYSTAL STRUCTURE OF WATKINSONITE, $Cu_2PbBi_4Se_8$, FROM THE ZÁLESÍ URANIUM DEPOSIT, CZECH REPUBLIC

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ABSTRACT

The crystal structure of sulfur-free watkinsonite, ideally $Cu_2PbBi_4Se_8$, monoclinic, *a* 12.952(4), *b* 4.152(1), *c* 15.155(5) Å, β 108.93(1)°, space group $P2_1/m$, Z = 2, part of the selenide mineralization of the uranium deposit of Zálesí, Czech Republic, has been solved by direct methods and refined to $R_1 = 4.61\%$ on the basis of 1287 unique reflections [$F_o > 4\sigma(F_o)$] collected on a Bruker P3 diffractometer with a CCD detector and Mo*K*α radiation. The crystal structure contains one Pb site, four Bi sites, two Cu sites and eight Se sites. Partial replacement of one Cu (in a linearly coordinated site) by Ag is observed. The crystal structure consists of $(100)_{PbS}$ slabs four atomic planes thick of a galena-like structure alternating with single layers of hexagonally packed selenium. The Pb atoms form asymmetric bicapped coordination prisms embedded in the surfaces of the galena-like pseudotetragonal slabs; atoms Bi1–3 occur as irregular coordination octahedra in the interior and at the surfaces of this slab. In addition, Bi4 forms a coordination prism similar to that of lead. Tetrahedrally coordinated copper Cu2 caps triangular voids of the hexagonal layer, whereas linearly coordinated Cu1 (with minor Ag), with the opposing Cu–Se bonds equal to 2.36 and 2.40 Å, respectively, forms foreshortened coordination octahedra, with four additional Cu–Se distances in the range 3.05–3.17 Å. The crystal structure of watkinsonite is closely related to that of berryite, $Cu_3Ag_2Pb_3Bi_7S_{16}$, in which the foreshortened coordination octahedra are occupied by Ag, and Cu resides in the hexagonal layer.

Keywords: sulfosalt, watkinsonite, crystal structure, berryite, Zálesí deposit, Czech Republic.

SOMMAIRE

Nous avons résolu par méthodes directes la structure cristalline de la watkinsonite dépourvue de soufre, dont la formule, de façon idéale, est $Cu_2PbBi_4Se_8$, monoclinique, *a* 12.952(4), *b* 4.152(1), *c* 15.155(5) Å, β 108.93(1)°, groupe spatial $P2_1/m$, Z = 2, formant partie de la minéralisation en séléniures du gisement uranifère de Zálesí, en République Tchèque, et nous l'avons affinée jusqu'à un résidu R_1 de 4.61% en utilisant 1287 réflexions uniques observées [$F_o > 4\sigma(F_o)$], prélevées avec un diffractomètre Bruker P3 muni d'un détecteur CCD et avec rayonnement Mo*K*α. La structure contient un site Pb, quatre sites Bi, deux sites Cu et huit sites Se. Nous observons le remplacement partiel d'un atome de Cu (dans un site à coordinence linéaire) par Ag. La structure cristalline est faite de dalles de $(100)_{PbS}$ d'une épaisseur de quatre plans atomiques, dont la structure ressemble à celle de la galène, qui alternent avec des couches distinctes de sélénium en agencement compact hexagonal. Les atomes de Pb logent dans des prismes de coordinence assymétriques et biterminés, encastrés dans la surface des dalles pseudotétragonales ressemblant à la galène; les atomes Bi1–3 se trouvent en coordinence octaédrique irrégulière à l'intérieur et à la surface de ces dalles. De

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plus, l'atome Bi4 forme un prisme de coordinance semblable à celui qui renferme le Pb. Le Cu2, à coordinence tétraédrique, recouvre des lacunes triangulaires de la couche hexagonale, tandis que le Cu1 (avec un faible quantité de Ag), en coordinence linéaire, les liaisons Cu–Se étant égales à 2.36 et 2.40 Å, respectivement, forment des octaèdres de coordinence trappus ayant quatre liaisons Cu–Se additionnelles dans l'intervalle 3.05–3.17 Å. La structure cristalline de la watkinsonite montre une relation étroite avec celle de la berryite, $Cu_3Ag_2Pb_3Bi_7S_{16}$, dans laquelle Ag occupe les octaèdres de coordinence trappus, et le Cu réside dans la couche hexagonale.

(Traduit par la Rédaction)

Mots-clés: sulfosel, watkinsonite, structure cristalline, berryite, gisement de Zálesí, République Tchèque.

INTRODUCTION

Watkinsonite is a selenosulfide of lead, bismuth and copper, first described by Johan *et al.* (1987) from the selenide–telluride association of the Otish Mountains uranium deposit, Quebec, Canada. The empirical formula, $Cu_{2.36}Pb_{1.26}Bi_{3.70}Se_{6.21}S_{1.74}Te_{0.05}$, was approximated as $Cu_2PbBi_4(Se,S)_8$ (Förster *et al.* 2005). The original crystallographic data indicate that watkinsonite is monoclinic, space group *P*2/*m*, *P*2, or *Pm*, with *a* 12.921, *b* 3.997, *c* 14.989 Å, and β 109.2°. A new find of virtually sulfur-free watkinsonite from the Zálesí uranium deposit, Czech Republic, yielded material suitable for a crystal-structure analysis.

In the paper on the crystal structure of berryite, $Cu_3Ag_2Pb_3Bi_7S_{16}$, Topa *et al.* (2006) suggested that watkinsonite ought to be structurally related to the monoclinic polytype of berryite they analyzed, because its d_{001} value (equal to 14.16 Å) is a half of the corresponding spacing (28.24 Å) in berryite, and the published unit-cell of watkinsonite is metrically identical to one of the two "component subcells" recognizable for the two variants of the pseudotetragonal layer (plus adjacent interlayer) in the structure of berryite–$P2_1/m$. This prediction has now been confirmed to a surprising extent.

MATERIAL INVESTIGATED

The scarce samples containing watkinsonite were collected from the waste pile of the mine dump material that probably originated from Adit No. 1 of the uranium mine, or from unnamed exploratory shafts in the area of the small uranium deposit of Zálesí. This deposit is situated at the southern margin of the settlement of Zálesí, about 6.5 km southwest of the Rychlebské Hory Mountains, northern Moravia, Czech Republic. A relatively abundant selenide mineralization is associated with the older, uraninite stage of mineralization that is close to the so-called "five-elements" formation (U–Ni–Co–As–Ag) of hydrothermal ore veins (Fojt *et al.* 2005, Sejkora *et al.* 2006). Watkinsonite occurs there as irregular aggregates from 0.01 to about 4 mm, usually smaller than 0.5 mm. On a fresh fracture, it is yellowish to brownish grey (in comparison with clausthalite); it exhibits a metallic luster and a characteristic conchoidal fracture. Watkinsonite aggregates in a quartz gangue are usually intergrown with practically sulfur-free clausthalite $(Pb_{0.97}Ag_{0.01}Cu_{0.01}Bi_{0.01})_{\Sigma 1.00}Se_{0.99}$ (Fig. 1); uraninite, chalcopyrite, bornite, covellite, löllingite and S-rich umangite were also observed in close association.

EXPERIMENTAL

Chemical analyses

Quantitative chemical data for watkinsonite were obtained on two different electron microprobes. Initially, at the Laboratory of Electron Microscopy and Microanalysis of Masaryk University and Czech Geological Survey, Brno, watkinsonite (15 aggregates) and associated minerals were analyzed with a Cameca SX–100 electron microprobe in the wavelength-dispersion mode (WDS) with an accelerating voltage of 25 kV, a specimen current of 20 nA, and a beam diameter of about 1 μm. The following standards and X-ray lines were used: Cu (Cu Kα), Ag (Ag Lα), PbSe (Se Lβ), $CuFeS_2$ (S*K*α), Bi_2Te_3 (Te*L*β), PbS (Pb*M*α) and Bi (Bi*M*β). Peak-counting times (CT) were 20 s for both main and minor elements; CT for each background was one half of peak time. Raw intesities were converted to the concentrations automatically using the *PAP* (Pouchou & Pichoir 1985) matrix-correction software package.

At the Department of Geography and Geology, University of Salzburg, a JEOL Superprobe JXA–8600 apparatus was operated in WDS mode, at 25 kV and 35 nA, with a defocused beam (~3 μm). The measurement time was 15 s for peak and 5 s for background counts. The following standards and X-ray lines were used: natural $CuFeS_2$ (chalcopyrite; Cu*K*α), natural PbS (galena Pb*L*α), synthetic Bi_2Se_3 (Bi*L*α, Se*L*α), synthetic Bi_2S_3 (S*K*α), synthetic CdTe (Te*L*α) and Ag metal (Ag*L*α). The raw data were corrected with the on-line ZAF–4 procedure. Chemical data on the grain presented in Figures 1a and 1b, together with selected results of point analyses made in Brno, are shown in Table 1 and Figure 2. In the (Cu + Ag) – Bi – Pb diagram, the chemical composition of watkinsonite from Zálesí is positioned close to the structurally determined formula $Cu_2PbBi_4Se_8$.

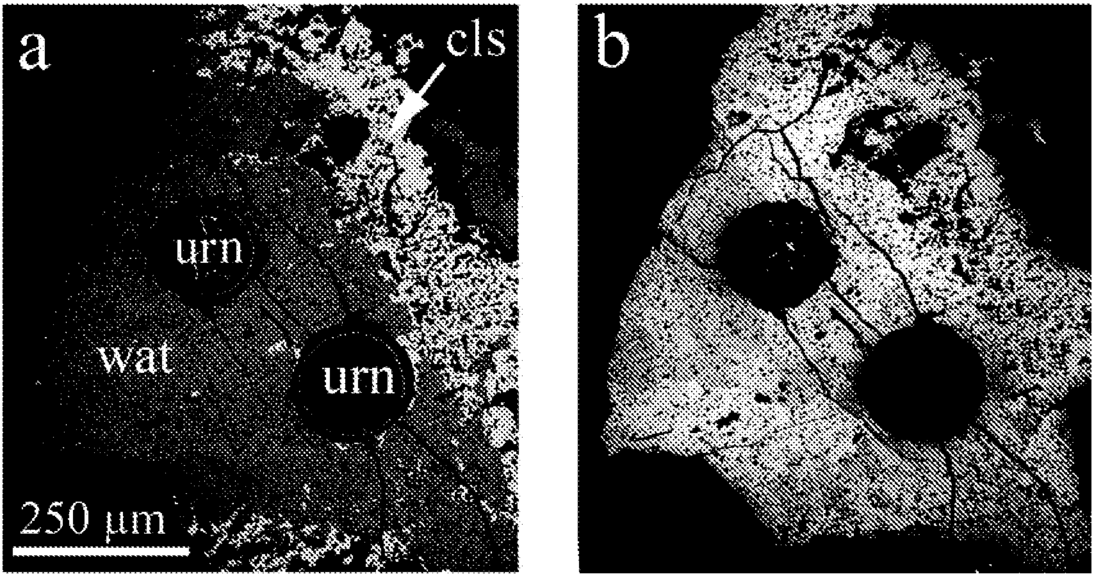

FIG. 1. Back-scattered electron image (a) and optical image (b) of the grain of watkinsonite studied from Zálesí, Czech Republic. Symbols: wat: watkinsonite, cls: clausthalite, urn: uraninite.

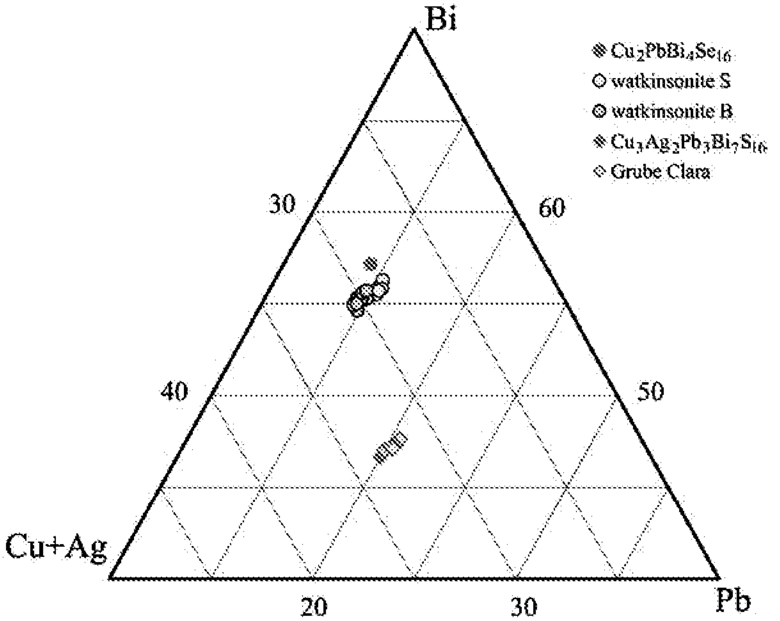

FIG. 2. Chemical composition of watkinsonite from Zálesí (circles) and berryite from Grube Clara (Topa *et al.* 2006) (rhombs) in the central portions of the (Cu + Ag) – Bi – Pb diagram.

TABLE 1. CHEMICAL COMPOSITION OF WATKINSONITE FROM ZÁLESÍ

	measured	NA	Cu	Ag	Pb	Bi	Se	Te	S	total
1	Brno	14	6.80(15)	1.18(17)	11.97(16)	45.11(51)	34.38(44)	0.00(00)	0.08(06)	99.51(45)
2	Salzburg	8	6.32(18)	1.25(20)	12.30(11)	45.01(22)	34.43(22)	0.08(04)	0.08(03)	99.47(19)

1) $Cu_{1.93}Ag_{0.20}Pb_{1.04}Bi_{3.90}S_{0.05}Te_{0.00}Se_{7.87}$ 2) $Cu_{1.81}Ag_{0.21}Pb_{1.08}Bi_{3.92}S_{0.05}Te_{0.01}Se_{7.92}$

NA: number of point analyses, compositions are reported in wt.%. Empirical formulae were calculated on the basis of 15 atoms *pfu*.

Single-crystal X-ray diffraction

For our single-crystal investigation, several grains of watkinsonite were extracted from the aggregates in a polished section. They were investigated with a Bruker AXS diffractometer equipped with a CCD area detector using graphite-monochromated Mo*K*α radiation. An irregular fragment measuring approximately 0.03 × 0.05 × 0.09 mm was found to be suitable for structural investigation. Experimental data are listed in Table 2. The SMART (Bruker AXS, 1998) system of programs was used for unit-cell determination and data collection, SAINT+ (Bruker AXS, 1998) for the calculation of integrated intensities, and XPREP (Bruker AXS, 1998) for empirical absorption-correction based on pseudo-Ψ scans. The space group $P2_1/m$, proposed by the XPREP program, differs from the original proposal derived from powder data by Johan *et al.* (1987). The structure of watkinsonite was solved by direct methods (program SHELXS of Sheldrick 1997a) and difference-Fourier syntheses (program SHELXL of Sheldrick 1997b). Refinement data are given in Table 2; fractional coordinates and anisotropic displacement-parameters of atoms are listed in Table 3. The principal interatomic distances are presented in Table 4, and selected geometrical parameters for individual coordination polyhedra, calculated with the IVTON program (Balić-Žunić & Vicković 1996), are given in Table 5. A table of structure factors for watkinsonite may be obtained from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Watkinsonite CM48_1109]. Atom labeling is shown in Figure 3, and the crystal structure is illustrated in Figure 4.

TABLE 2. SINGLE-CRYSTAL X-RAY DIFFRACTION: EXPERIMENTAL AND REFINEMENT DETAILS CONCERNING WATKINSONITE

Crystal data			
Chemical formula	$Cu_2PbBi_4Se_8$	Unit-cell dimensions	
Formula weight	1801.9	a (Å)	12.952(4)
Crystal system	Monoclinic	b	4.1523(14)
Space group	$P2_1/m$	c	15.155(5)
		β (°)	108.931(5)
D_x (Mg m^{-3})	7.76	V (Å^3)	770.9(8)
No. of reflections for cell parameters	1215	Z	2
		Crystal form	irregular
μ (mm^{-1})	77.91	Crystal color	black
Crystal size (mm)	0.03 × 0.05 × 0.09		
Data collection			
T_{min}, T_{max}	0.1319, 0.8060		
No. of measured reflections	6621		
No. of independent reflections	2000		
No. of observed reflections	1287 for $F_o > 4\sigma(F_o)$		
Criterion for observed reflections	$I > 2\sigma(I)$		
R_{int}	15.75%		
θ_{max} (°)	28.3		
Range of h, k, l	$-17 \le h \le 16$, $-4 \le k \le 5$, $-20 \le l \le 19$		
Refinement			
Refinement on F_o^2			
$R_1[F_o > 4\sigma(F_o)]$ (%)	4.61		
wR (F_o^2) (%)	8.80		
S (*GooF*)	0.774		
No. of reflections used	1287		
No. of parameters refined	79		
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0\,P)^2 + 0.0P]$ where $P = (F_o^2 + 2F_c^2)/3$		
$(\Delta/\sigma)_{max}$	0.031		
$\Delta\rho_{max}$ (e/Å^3)	3.83 [0.74 Å from Bi3]		
$\Delta\rho_{min}$ (e/Å^3)	–3.00 [1.23 Å from Se5]		
Extinction coefficient	0.00012(5)		
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)		
Computer programs			
Structure solution	SHELXS97 (Sheldrick 1997a)		
Structure refinement	SHELXL97 (Sheldrick 1997b)		

DESCRIPTION OF THE STRUCTURE

General features

The structure of watkinsonite can be described in analogy to that of berryite (Topa *et al.* 2006) as an alternation of two types of layer, *i.e.*, pseudotetragonal slabs that are four atomic planes thick, and pseudohexagonal layers that in these structures are reduced to single sheets of hexagonally arranged anions with interstitial cations present in some positions of the sheet.

The structure contains one lead site, four independent Bi sites that do not seem to exhibit signs of Pb-for-Bi substitution, and two copper sites. One of the latter sites, the linearly coordinated Cu1 site, accommodates the minor Ag present. There are eight independent Se sites. All atoms are at the (*m*) positions with $y = 0.25$ and 0.75. Whether there is any partial order of Se and S in distinct sites of the two types of layer in the case of watkinsonite from Otish Mountains (Johan *et al.* 1987), similar to that observed for the layered structure of proudite (Mumme *et al.* 2009), is not known at present.

Coordination polyhedra

The *Cu1 site* is an octahedrally coordinated (2 + 4) site in the pseudotetragonal layer. The two bonds oriented to the foreshortened apices of the coordination octahedron form a linear coordination. The opposing Cu–Se distances involved are equal to 2.358 and 2.401 Å, respectively; the shorter of them is oriented toward the exterior of the pseudotetragonal layer. The *Cu1* site houses the bulk of analytically determined Ag (Tables 3, 4). The contents of silver in the structurally analyzed grain extracted from a margin of the watkinsonite aggregate appear slightly higher than the average obtained for the bulk (Table 1).

These paired octahedral *Cu1* sites are analogous to the paired octahedral *Ag1* sites in berryite–$P2_1/m$ (Topa *et al.* 2006), which have the short Ag–S bonds equal to 2.443–2.475 Å. In watkinsonite, the four long Cu1–Se distances in the octahedron are equal to 3.046–3.168 Å; those of Ag–S in berryite are 3.104–3.123 Å long. For an exact comparison with berryite, the difference between the radii of S^{2-} and Se^{2-} should be subtracted from the Cu–Se data.

The *Cu2* site is tetrahedrally coordinated (Table 4) and corresponds to the Cu2 site of berryite. Atom Cu2 forms [010] strings of edge-sharing tetrahedra, however,

TABLE 3. POSITIONAL AND ANISOTROPIC DISPLACEMENT PARAMETERS FOR WATKINSONITE FROM ZÁLESÍ

Atom	*x*	*z*	*sof*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
Pb	0.23691(7)	0.33139(8)		0.0288(3)	0.0255(5)	0.0174(5)	0.0438(8)	0.0117(5)
Bi1	0.04295(6)	0.88759(6)		0.0167(2)	0.0176(4)	0.0126(5)	0.0189(6)	0.0043(4)
Bi2	0.56525(6)	0.29021(6)		0.0161(2)	0.0152(4)	0.0128(5)	0.0193(6)	0.0042(4)
Bi3	0.70545(6)	0.90960(7)		0.0173(2)	0.0155(4)	0.0120(5)	0.0224(6)	0.0034(4)
Bi4	0.92454(7)	0.37818(7)		0.0213(3)	0.0187(4)	0.0167(5)	0.0257(6)	0.0031(4)
Cu1	0.3788(16)	0.9009(15)	0.68(3)	0.088(9)	0.060(9)	0.184(23)	0.025(11)	0.021(8)
Ag	0.3860(24)	0.9006(18)	0.32(3)	0.079(9)	0.109(19)	0.097(19)	0.007(11)	-0.012(10)
Cu2	0.47134(22)	0.53715(23)		0.0258(1)	0.030(2)	0.012(2)	0.037(2)	0.014(2)
Se1	0.12568(15)	0.50967(16)		0.0141(5)	0.0126(9)	0.013(1)	0.016(1)	0.004(1)
Se2	0.13530(15)	0.11562(16)		0.0152(5)	0.0127(9)	0.014(1)	0.017(1)	0.003(1)
Se3	0.30144(16)	0.73696(18)		0.0189(5)	0.0137(9)	0.013(1)	0.030(2)	0.007(1)
Se4	0.43836(16)	0.06837(18)		0.0185(5)	0.0173(9)	0.014(1)	0.026(2)	0.009(1)
Se5	0.61451(16)	0.70857(17)		0.0161(5)	0.0150(9)	0.012(1)	0.021(2)	0.006(1)
Se6	0.63573(15)	0.48096(17)		0.0151(5)	0.0135(9)	0.012(1)	0.018(1)	0.002(1)
Se7	0.80926(15)	0.11716(16)		0.0155(5)	0.0132(9)	0.013(1)	0.020(1)	0.004(1)
Se8	0.95263(15)	0.69674(16)		0.0136(5)	0.0136(9)	0.011(1)	0.015(1)	0.003(1)

$y = 0.25$, $U_{23} = U_{12} = 0$.

TABLE 4. SELECTED CATION–ANION DISTANCES (Å) IN WATKINSONITE FROM ZÁLESÍ

Pb-		Bi1-		Bi2-		Bi3-	
Se5	3.023(2) ×2	Se8	2.746(3)	Se6	2.735(3)	Se4	2.880(2) ×2
Se2	3.104(3)	Se7	2.841(2) ×2	Se3	2.815(2) ×2	Se5	2.888(3)
Se8	3.137(2) ×2	Se2	3.094(2) ×2	Se5	3.124(2) ×2	Se7	2.993(3)
Se1	3.450(3)	Se2	3.270(3)	Se4	3.228(3)	Se2	3.037(2) ×2
Se6	3.475(2) ×2						
Bi4-		Cu1-		Ag-		Cu2-	
Se1	2.718(2)	Se3	2.358(21)	Se3	2.364(25)	Se6	2.462(2) ×2
Se1	2.888(2) ×2	Se4	2.401(22)	Se4	2.410(26)	Se6	2.538(4)
Se8	3.050(2) ×2	Se4	3.069(15) ×2	Se4	3.002(19) ×2	Se5	2.657(3)
Se3	3.551(2) ×2	Se7	3.144(16) ×2	Se7	3.215(20) ×2		
Se7	3.748(3)						

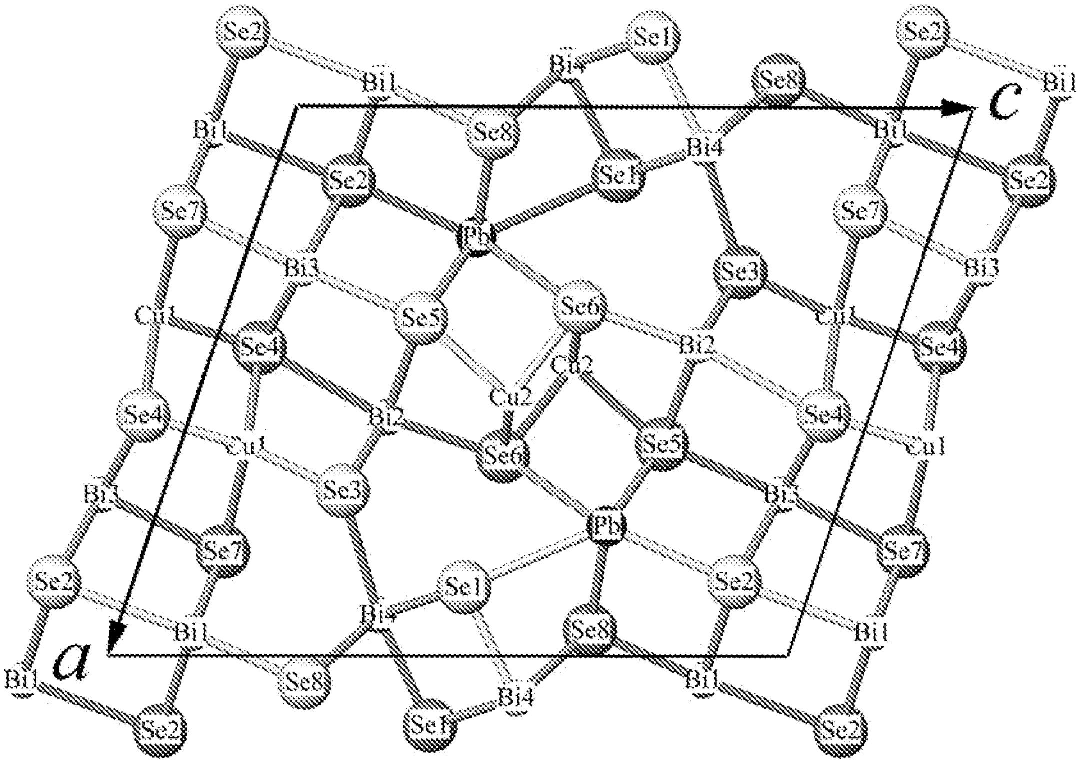

FIG. 3. Atom labels in the structure of watkinsonite. All sites are fully occupied.

with Cu–Cu distances equal to 2.58 Å, indicating Cu–Cu interactions. The marginal Bi octahedra of the pseudotetragonal layer, *Bi1* and *Bi2*, show a considerable difference between the Bi–Se distance in the apex of the pyramid and that below the base of the tetragonal pyramid: 2.746 *versus* 3.270 Å and 2.735 *versus* 3.228 Å, respectively. The *Bi4 site*, which forms paired columns of square coordination pyramids of Bi, is the most eccentric of all Bi sites, with the Bi–S bond toward the apex of the pyramid equal to 2.718 Å, opposed by the long distances inside the capped trigonal coordination prism (Fig. 4), which are equal to 3.551 and 3.748 Å, respectively. The *Bi3* site, occluded completely in the pseudotetragonal layer, is close to octahedral, with the apical distances equal to 2.888 and 2.993 Å, and a fairly symmetrical distribution of the remaining distances, from 2.880 to 3.037 Å. This results in an eccentricity value that is much lower than for the other Bi sites (Table 5). The polyhedron volume, however, is smallest of all the Bi sites (Table 5). This finding and the bond-valence results suggest that no recognizable Pb-for-Bi substitution takes place at the *Bi3* site.

TABLE 5. CHARACTERISTICS OF COORDINATION POLYHEDRA OF CATIONS IN WATKINSONITE FROM ZÁLESÍ

Atom	1	2	3	4	5	6	7	8
Pb	8	3.210	0.033	0.240	0.914	138.590	58.074	1.994
Bi1	6	2.991	0.014	0.292	0.987	112.058	35.169	3.328
Bi2	6	2.962	0.001	0.299	0.994	108.860	34.635	3.432
Bi3	6	2.952	0.004	0.123	0.991	107.778	34.187	3.260
Bi4	8	3.154	0.035	0.459	0.938	131.455	55.001	3.369
Cu1	6	2.863	0.045	0.063	0.606	98.281	29.872	0.972
Ag	6	2.863	0.045	0.149	0.606	98.281	29.872	1.842
Cu2	4	2.515	0.041	0.161	1.000	66.652	7.835	1.031

Columns: 1) coordination number, 2) radius r_s of a circumscribed sphere, least-squares-fitted to the coordination polyhedron, 3) "volume-based" distortion υ = [*V*(ideal polyhedron) – *V*(real polyhedron)] / *V*(ideal polyhedron); the ideal polyhedron has the same number of ligands, 4) "volume-based" eccentricity $ECC_V = 1 - [(r_s - \Delta)/r_s]^3$; Δ is the distance between the center of the sphere and the central atom in the polyhedron, 5) "volume-based" sphericity $SPH_V = 1 - 3\sigma_r r_s$; σ_r is the standard deviation of the radius r_s, 6) volume of the circumscribed sphere, 7) volume of the coordination polyhedron, 8) bond-valence sum.

The single *Pb* site is an asymmetric bicapped trigonal prism site, with out-of-layer Pb–Se distances being substantially longer than the intralayer ones (Table 4).

Modular description

The pseudotetragonal (Q) slabs four atomic layers thick are outlined schematically by shading in Figure 4. The pseudohexagonal (H) layers are single layers of Se atoms halving the interspace between the Q slabs. The Bi4 positions are protruding from the surfaces of the pseudotetragonal layers, with coordination polyhedra including three atoms from the hexagonal layers. The long Bi4–Se7 distance "ties" the Bi4 atom to the Q layer. This situation corresponds in full to that in berryite (Topa *et al.* 2006), in which the bismuth site involved is Bi1 (Fig. 5). In watkinsonite, two Bi4 sites are paired, but in berryite, Bi1 columns pair with Pb3 columns. As in berryite, watkinsonite is a *lock-in* type of incommensurate two-layer structure, in which one common period comprises two pseudohexagonal subcells matching three pseudotetragonal subcells along the layer in the *a* direction, and this ratio is fixed by interlayer bonds. In berryite (Fig. 5), the pseudohexagonal layer is populated by an alternation of Cu1, Cu2 and Cu3 coordination triangles; only the space occupied by the Bi1–Pb3 coordination polyhedra was left unfilled. In watkinsonite, both the space defined by the pair of Bi4–Bi4 polyhedra and that facing Pb are left empty, and only single [010] columns of this layer are occupied by Cu, in a compact manner. The presence of two Cu sites instead of three as in berryite is balanced out by the substitution of Pb3 in berryite by Bi4 in watkinsonite.

According to the cations protruding from the surface of the Q layer, the sequence of Q layers in berryite–$P2_1/m$ was described by Topa *et al.* (2006) as an alternation of "pseudotetragonal Pb–Pb layers" (with Pb3 protruding) with "pseudotetragonal Bi–Bi layers" (Bi1 protruding). They also argued that in the orthorhombic–$Pcm2_1$ polytype of berryite, the layers ought to be of the "Pb–Bi type". Based on the original space-group assignment by Johan *et al.* (1987), Topa *et*

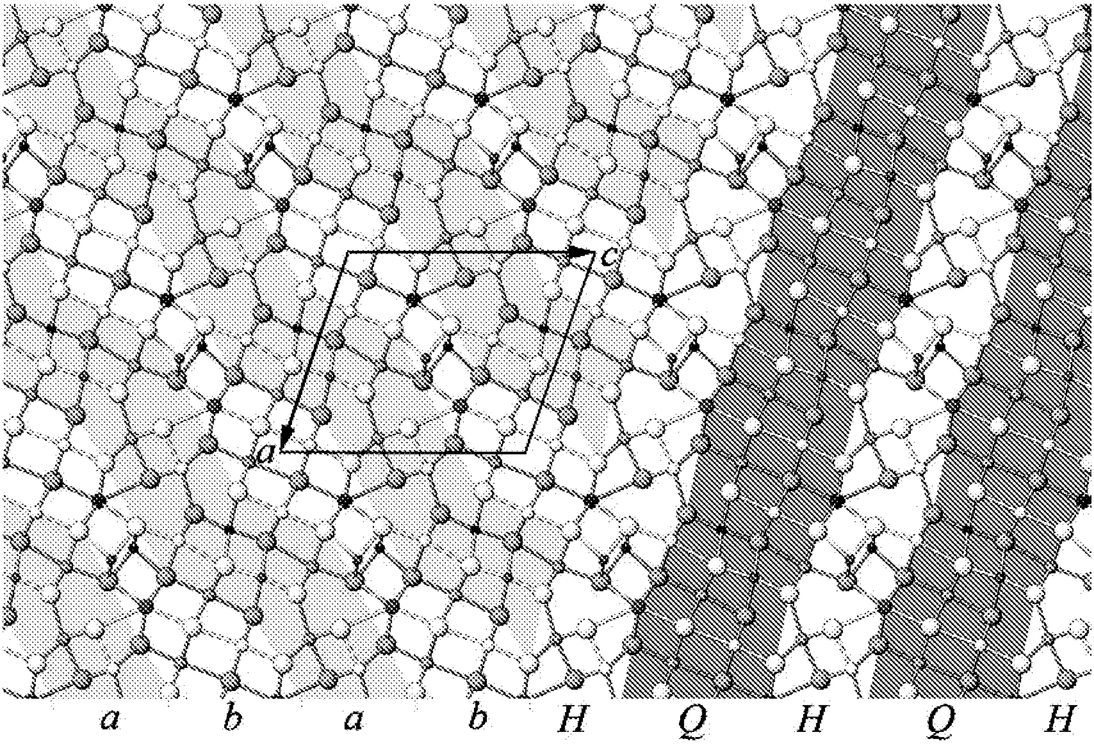

FIG. 4. The crystal structure of watkinsonite. In the order of decreasing size, spheres represent Se, Pb (blue), Bi, and Cu (red). The pseudotetragonal layers (*Q*) and the pavonite-related layers "*a*", respectively, are shaded; the intervening pseudohexagonal (*H*) layers and the intermediate "*b*" intervals are left unshaded. In order to identify the single-sheet *H* layers, follow the pattern and spacing of Se atoms in the unshaded interspaces between two adjacent *Q* layers. Inspection of the Figure 5 will help as well.

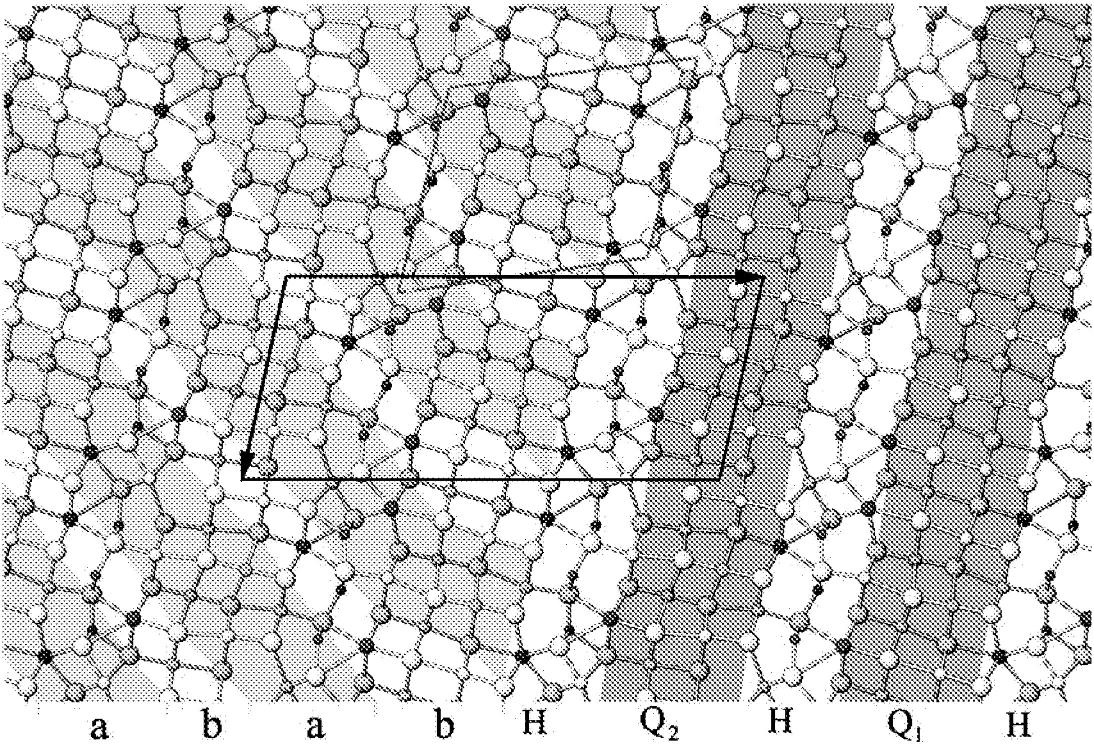

FIG. 5. The crystal structure of the monoclinic polytype of berryite (Topa *et al.* 2006). For the majority of explanations, see the caption to Figure 4. The silver atoms are indicated in green. The component subcell centered on the Q_1 layers (Pb–Pb type, see the text), metrically identical to the unit cell of watkinsonite, is drawn in red.

al. (2006) assumed that the layers in watkinsonite also are of the "Pb–Bi type", and the original space-group *Pn* was considered as the probable choice. The present data, however, indicate that the symmetry is $P2_1/m$, and the layers are of the "Bi–Bi type", although the unit-cell metric corresponds to that of the "Pb–Pb" subunit of berryite, illustrated in the central upper portions of Figure 3 in Topa *et al.* (2006).

Lone-electron-pair micelles in watkinsonite and berryite are of the same type and position: the micelle defined by two Bi1 and two Bi3 atoms in the interior of the Q slab of watkinsonite (Fig. 4) is the same as the 2 Bi3 – 2 Bi7 micelle in berryite (Fig. 5), and the spaces that accommodate pairs of lone electrons under Bi4 coordination pyramids in watkinsonite correspond to such spaces under Bi1 polyhedra in berryite. All pairs of Cu1 coordination octahedra have the same orientation in the structure of watkinsonite, but the corresponding pairs of Ag sites alternate in orientation in monoclinic berryite (Figs. 4, 5).

The distribution of copper

The presence of linearly coordinated Cu (with only minor Ag) in the form of paired flattened $Cu2Se_6$ octahedra in watkinsonite was an unexpected feature of its structure, and it resolves speculations about the accommodation of copper in this mineral. As a result of this finding, the configuration of the Q layer in watkinsonite is exceedingly close to that of the "Pb–Pb" layer in monoclinic berryite. The only difference is that the protruding atoms on layer surfaces are Bi4 in watkinsonite as opposed to Pb in berryite. The other Pb site on the Q surface is common to both structures and also to both types of layer in berryite.

The presence of smaller coordination-octahedra of Cu in the Q layer of watkinsonite (in comparison to the rest of the structure), instead of the Ag octahedra found in berryite, has a pronounced influence on the distribution of Cu in the adjacent hexagonal layer. The coordination triangles that correspond to "Cu1" and "Cu3" positions of berryite lie in the extension of the space occupied by the octahedrally coordinated Cu1 in

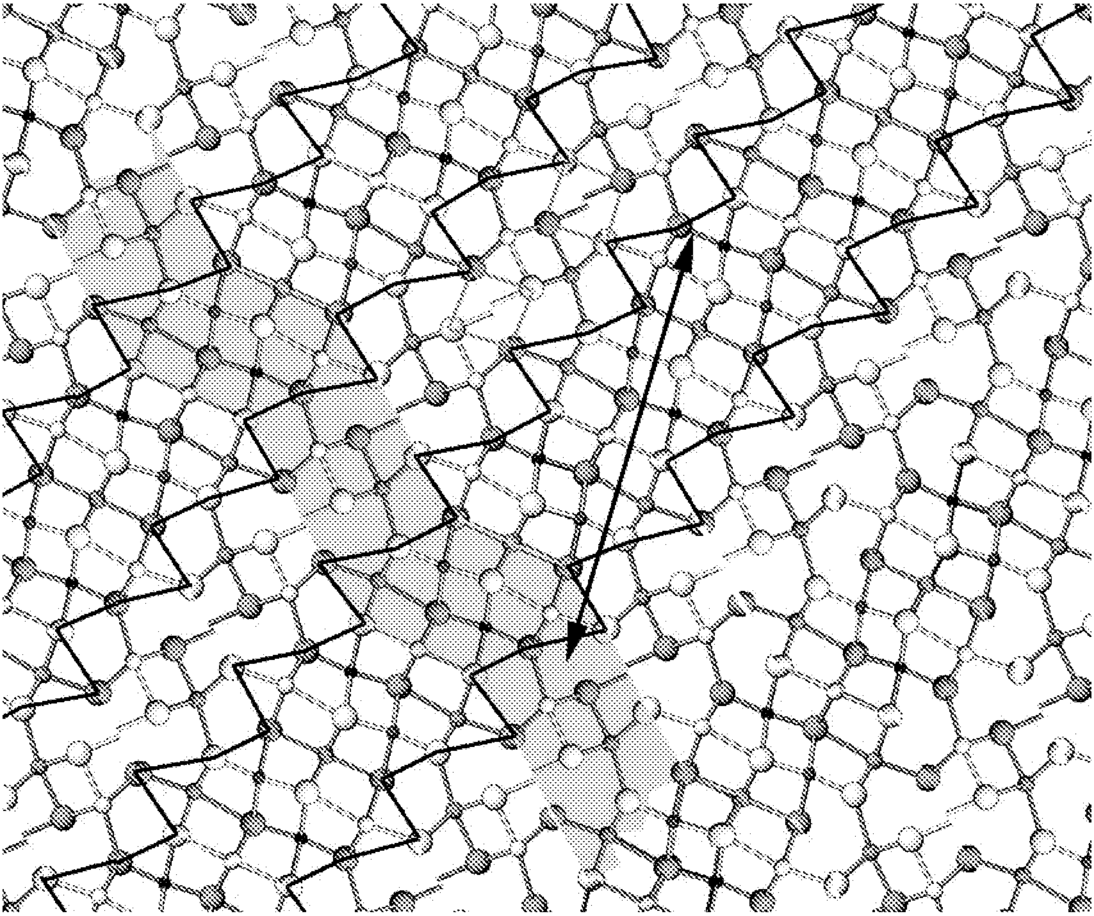

FIG. 6. Collage of slices of pavonite-like structure (one of which is shaded) cut out of the structure of watkinsonite. When joined by applying crystallographic shear, they generate a pavonite homologue N = 5. Selected foreshortened octahedra are indicated in pink.

watkinsonite. Thus, the relevant coordination triangles, which were occupied in berryite, become too small to host a copper site. Copper is then forced to populate the Cu2 site, which corresponds to the "Cu2" position of berryite.

RELATIONS TO OTHER SULFOSALTS

In addition to the obvious modular affinity to the sulfosalts related to cannizzarite, such as berryite, watkinsonite is also related to the pavonite homologous series (Makovicky *et al.* 1977). If we divide the structure of watkinsonite into slices compatible with the pavonite structural principle (slices denoted as *a* and shaded in Fig. 6) and remove the intermediate parts (slices *b*, unshaded) by means of crystallographic shear, a structure of the pavonite homologue N = 5 will result. It has paired Bi pyramids and empty coordination octahedra in the thinner layers of the ^{5}P structure, and it has five octahedra strung along diagonals of the thicker structural layers of this structure. The same exercise gave a more complicated homologue of pavonite, with N = 5, 6, 5 ,6… for berryite–$P2_1/m$ (Topa *et al.* 2006).

CONCLUSIONS

With the exception of one empty copper site (the two Cu sites Cu1 and Cu3 from berryite become equivalent in watkinsonite) and replacement of a marginal Pb atom by Bi, the structure of watkinsonite corresponds closely to that of the pseudotetragonal "Pb–Pb" layer of monoclinic berryite–$P2_1/m$, with the relevant parts of interlayer space and of the adjacent pseudohexagonal layer added, as predicted by Topa *et al.* (2006) (Figs. 4, 5). Thus it is one more success story of modular crystallography of sulfosalts. The most remarkable feature of the structure is the linear coordination of copper in the paired, foreshortened Cu1–Se_6 coordination octahedra in the pseudotetragonal portions of the structure. This unusual coordination is closer to that of Ag^+ and Hg^{2+} than to the usual tetrahedral or trigonal-planar Cu coordination observed in numerous sulfosalts. This structure type spans a range of compositions from mixed sulfide–selenide to pure selenide, and can contain different Cu:Ag proportions in the foreshortened octahedral sites.

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