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DANTOPAITE, $Ag_5Bi_{13}S_{22}$, THE ^{6}P NATURAL MEMBER OF THE PAVONITE HOMOLOGOUS SERIES, FROM ERZWIES, AUSTRIA

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Abstract

Dantopaite, $Ag_5Bi_{13}S_{22}$, is the ^{6}P natural member of the pavonite homologous series. It is a very rare mineral in a quartz vein hosted by Variscan metagranitoids at the abandoned mining district at Erzwies, Gasteiner Valley, province of Salzburg, Austria. The associated sulfosalts are lillianite–gustavite, heyrovskyite, eskimoite, vikingite, ourayite, bismuthinite, krupkaite, benjaminite, pavonite, and cosalite. Traces of pyrite, tetradymite and native gold also are present. The new species occurs as isolated grains intimately intergrown with pavonite or benjaminite or both. The grain size does not exceed 250–300 μm. Dantopaite has a greyish white color and is opaque. It has a metallic luster and a grey streak. Its hardness (VHN_{50}) is ~190 kg/mm^2 (3½ on the Mohs scale). In plane-polarized light, and compared to galena, it is weakly bireflectant, and distinctly pleochroic in shades of grey. The anisotropy is distinct in air and oil, and the rotation tints change from greyish blue to brownish grey. The reflectances (in air) are tabulated. The average result of electron-microprobe analysis is: Cu 1.68, Ag 11.56, Pb 4.64, Bi 63.82, Te 0.34, S 17.52, total 99.57 wt.%, which gives $Cu_{1.06}Ag_{4.24},Pb_{0.9}Bi_{12.23}S_{21.89}Te_{0.11}$. The ideal formula is $Ag_5Bi_{13}S_{22}$. Dantopaite is monoclinic with *a* 13.380(3), *b* 4.0492(9), *c* 18.690(4) Å, *V* 975.8(4) Å^3, space group *C*2/*m* and *Z* = 1. The calculated density is 6.74 g/cm^3. The strongest eight lines in the (calculated) powder-diffraction pattern [*d* in Å(I)(*hkl*)] are: 3.578(58)($\bar{2}05$), 3.452(90)(112), 3.331(36)($\bar{4}01$), 3.301(40)(204), 2.861(100)($\bar{3}13$), 2.225(24)($\bar{1}17$), 2.025(25)(020) and 2.013(24)(512). The crystal structure, based on 1051 observed reflections (R_1 = 7.3%), is that of N = 6 pavonite homologue, consisting of thick slabs with a width of six octahedra on a diagonal, in alternation with thin slabs composed of foreshortened octahedra and pairs of Bi coordination pyramids. The central columns of the thin structural slabs are populated by octahedrally coordinated Ag sites and tetrahedrally coordinated Cu1 and Cu2 sites; all of them are only partly occupied. In the thick slabs, with distorted octahedral bismuth sites, silver partly replaces bismuth in the centrally placed octahedra. The name honors Dr. Dan Topa (University of Salzburg), ore mineralogist and crystallographer.

Keywords: dantopaite, sulfosalt, new mineral species, pavonite homologue (^{6}P), silver, bismuth, crystal structure, Erzwies, Austria.

Sommaire

Nous décrivons la dantopaïte, $Ag_5Bi_{13}S_{22}$, le membre ^{6}P naturel de la série d'homologues de la pavonite. Il s'agit d'un minéral rarissime découvert dans une veine de quartz recoupant un métagranite d'âge varisque dans le camp minier abandonné de Erzwies, vallée de Gasteiner, province de Salzburg, en Autriche. Lui sont associés les sulfosels lillianite–gustavite, heyrovskyite, eskimoïte, vikingite, ourayite, bismuthinite, krupkaïte, benjaminite, pavonite, et cosalite. Des traces de pyrite, tétradymite et or natif sont aussi présentes. La nouvelle espèce minérale se présente en grains isolés en intercroissance intime avec la pavonite ou la benjaminite ou les deux. La taille des grains ne dépasse pas 250–300 μm. La dantopaïte est blanc grisâtre et opaque. Elle possède un éclat métallique et une rayure grise. La dureté (VHN_{50}) est ~190 kg/mm^2 (3½ sur l'échelle de Mohs). En lumière réfléchie, et comparée à la galène, la dantopaïte est faiblement biréflectante, et pléochroïque en teintes de gris. L'anisotropie est distincte dans l'air et dans l'huile, et les teintes de rotation changent du bleu grisâtre au gris brunâtre. Nous fournissons les réflectances dans l'air. En moyenne, les analyses avec une microsonde électronique ont donné Cu 1.68, Ag 11.56, Pb 4.64, Bi 63.82, Te 0.34, S 17.52, pour un total de 99.57% (poids), ou $Cu_{1.06}Ag_{4.24},Pb_{0.9}Bi_{12.23}S_{21.89}Te_{0.11}$. La formule idéale est $Ag_5Bi_{13}S_{22}$. La dantopaïte est monoclinique, avec *a* 13.380(3), *b* 4.0492(9), *c* 18.690(4) Å, *V* 975.8(4) Å^3, groupe spatial *C*2/*m* et *Z* = 1. La densité calculée

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est 6.74 g/cm^3. Les huit raies les plus intenses du spectre de diffraction (calculé) d'une poudre [d en Å(I)(hkl)] sont: 3.578(58) $(\bar{2}05)$, 3.452(90)(112), 3.331(36)$(\bar{4}01)$, 3.301(40)(204), 2.861(100)$(\bar{3}13)$, 2.225(24)$(\bar{1}17)$, 2.025(25)(020) et 2.013(24)(512). La structure cristalline, fondée sur 1051 réflexions observées (R_1 = 7.3%), est celle d'un homologue N = 6 de la pavonite, avec d'épais modules d'une largeur de six octaèdres en diagonale, en alternance avec des modules plus minces d'octaèdres plus trappus et de paires de pyramides où logent les atomes de Bi. Les colonnes centrales de ces modules plus minces sont peuplées de sites Ag à coordinence octaédrique et des sites Cu1 et Cu2 à coordinence tétraédrique. Tous ces sites ont un taux d'occupation incomplet. Dans les modules plus épais, ayant les sites octaédriques difformes de Bi, les atomes de Ag remplacent le Bi dans les octaèdres centraux. Le nom honore Dan Topa, de l'Université de Salzburg, minéralogiste des minerais et cristallographe.

(Traduit par la Rédaction)

Mots-clés: dantopaïte, sulfosel, nouvelle espèce minérale, homologue de la pavonite (^{6}P), argent, bismuth, structure cristalline, Erzwies, Autriche.

INTRODUCTION

In homologous series of minerals, members with certain values of the order number N may be very common, whereas other members, with N values interspersed between the common ones, may be rare or unknown. This has been the situation of the N = 6 homologue of the pavonite homologous series, situated crystal-chemically between the most common members, N = 5 (pavonite) and N = 7 (benjaminite). Therefore, the find of a natural N = 6 member, dantopaite, in the Siglitz – Bockhart – Erzwies ore district, Gasteinertal, province of Salzburg, Austria, provides evidence of the exceptional character of this sulfosalt occurrence. Dantopaite was found during field studies that constitute part of a larger project concerning the ore petrology and the conditions of formation of Alpine-type mesothermal gold mineralization (Paar 2006, Günther *et al.* 2000, Weber 1997). During the mapping of the structurally controlled mineralization at Erzwies ("ore meadow"), numerous outcrops of quartz veins were located, which contain a widespread distribution of patchy sulfosalts in association with high-grade gold and silver ore. In only one of the exposed veins, dantopaite occurs as rare inclusions in quartz in association with native gold and other sulfosalts and sulfides.

The new mineral species is named after Dr. Dan Topa (born 1955), in recognition of his outstanding contributions to the crystal chemistry and structures of sulfosalts, especially in regard to the pavonite series and bismuthinite derivatives. The new species and its name have been approved by the CNMNC of the IMA (2008–058). The holotype material (one polished section and a single-crystal mount) were deposited in the reference collection of the Department of Materials Research and Physics (Division of Mineralogy), University of Salzburg.

LOCATION AND GEOLOGY

The area of Erzwies, where mining for precious and base metals probably began long before the Middle Ages, is located in the Hohe Tauern region west of the Gasteinertal, in the province of Salzburg, Austria. It is situated in the direct northern continuation of the district of Siglitz–Bockhart which, together with other districts in the same region (Radhausberg, Hoher Goldberg, Goldzeche), were economically the most important centers of gold mining in the Alps. The mining area at Erzwies (Fig. 1) reaches from the Bockhartscharte in the south (2450 m above sea level) for more than 2 km toward the Angertal, where one encounters the lowermost adit (2200 m a.s.l.) used for drainage of the mine.

Signs of old mining activities, which lasted for several centuries, occur in a strip 500 m wide in a NNE direction, roughly parallel with the main ore-hosting structure (the "Kupelwieser" structure). The host rocks are metamorphosed Jurassic limestone and dolostone, which show widespread karstification. The extent of the mineralized system along strike is more than 4 km; the width of the veins, which pinch and swell, varies strongly. The ore assemblage of the prominent veins is typically composed of silver-rich native gold, arsenopyrite, pyrite, variable amounts of sphalerite, galena, Ag-rich tetrahedrite, acanthite and rare pyrargyrite. The gangue may be quartz, ankerite and intermediate Mn-bearing members of the magnesite–siderite solid solution.

In contrast to this type of mineralization is a system of numerous (~70) east–west-trending quartz veins. Outcrops can be observed at an elevation between 2440 and 2200 m above sea level. These veins penetrate Variscan granitoids (the "Central gneiss"), and have a thickness varying between a few centimeters and almost half a meter. Their continuation along strike and dip is strongly reduced, and is in the range of a few tens of meters (strike) and only meters (dip). They are cut by the above-described NNE-trending systems of veins, and thus older than it. At least five of these east–west-striking veins carry a very distinctive, and in places, rich sulfosalt mineralization. The striking indicator of this sulfosalt mineralization is pyrite in modified cubes up to 10 cm across, as well as irregular sandy accumulations of the same mineral. In superficially weathered portions of the veins, pyrite leaves hollow casts displaying its typical habit.

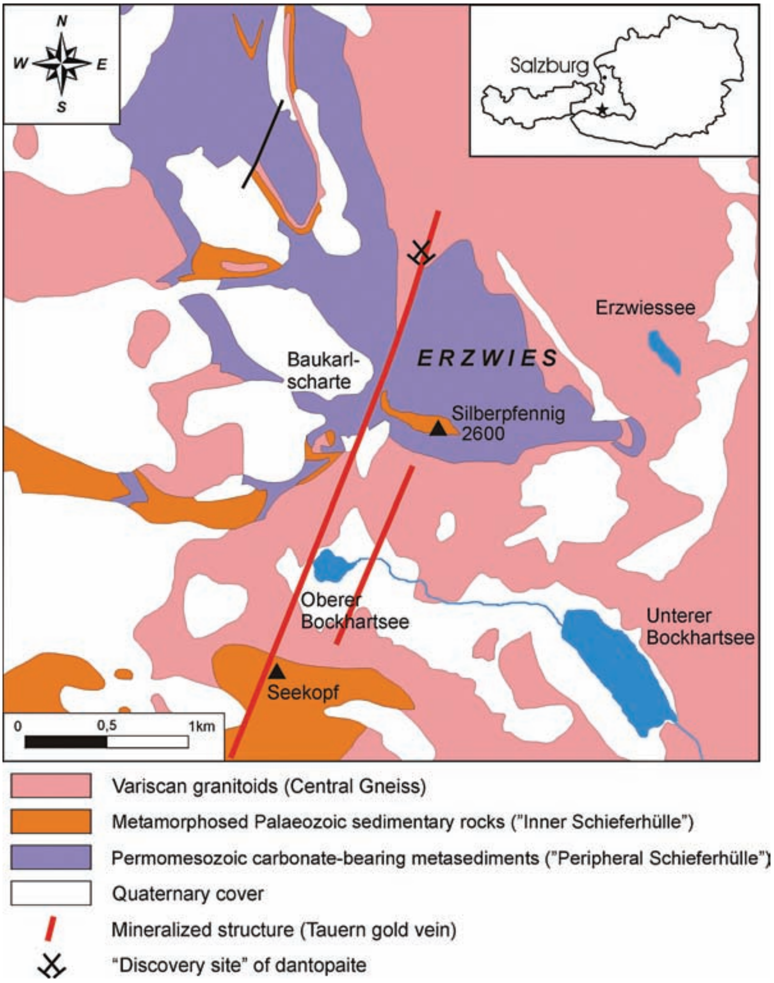

FIG. 1. The geological map of the Erzwies area and the location of the dantopaite occurrence.

OCCURRENCE OF DANTOPAITE

The type locality of the new sulfosalt species is a small exploration trench and a tunnel (20 m long) driven a few meters below the trench to explore the expected downward continuation of the mineralization. The location is situated on the orographic left-hand side of a steep flank that parallels the Kupelwieser main structure at an elevation of 2275 m a.s.l. The quartz vein exposed just above the nearly collapsed entrance of the tunnel contains gold-bearing arsenopyrite and pyrite. The thickness of the quartz vein is 0.2 m, the ore is concentrated in a massive band 2–5 cm wide. A parallel quartz veinlet less than 6 cm in thickness contains a sporadic sulfosalt mineralization in quartz, which in its richest part is composed of prismatic crystals reaching several centimeters. This subtype of sulfosalt mineralization (denoted as SS1 in the above studies) is represented by traces of dantopaite and members of the lillianite homologous series (LHS) such as gustavite, eskimoite, and ourayite, among others.

A few meters below the adit of the tunnel, loose blocks of another type of quartz occur, whose primary source could not be located. This is a smoky quartz variety, more coarse-grained than the quartz of the vein. It contains small vugs and carries plenty of muscovite. Dantopaite and other sulfosalts are concentrated in small amounts near the boundary with gneiss, which hosts the quartz vein. The mineralogy of this type of sulfosalt mineralization is distinctly different from that present in SS1. Here, dantopaite is accompanied by derivatives of the bismuthinite–aikinite series (bismuthinite, krupkaite), by members of the pavonite homologous series (PHS below) (pavonite, benjaminite), and also members of the lillianite homologous series (gustavite, heyrovskyite), cosalite, traces of tetradymite, native gold and pyrite. All the minerals mentioned in this section have been identified by ore microscopy and electron-microprobe analyses.

APPEARANCE AND PHYSICAL PROPERTIES

In polished sections, dantopaite is a relatively rare constituent. It occurs as independent grains (200–300 μm) embedded in quartz, and as a component of intergrowths with pavonite and benjaminite (Fig. 2). The latter occur as irregular, elongate polyphase grains with pavonite at one end, one or more grains of dantopaite in the central parts, and benjaminite grains at the other end (Figs. 2a, b). They are enclosed in quartz and appear slightly corroded on most surfaces, making genetic interpretations uncertain. Pavonite and benjaminite may be polysynthetically twinned. A grain of dantopaite with lamellae of benjaminite has been located as well (Fig. 2c).

Benjaminite associated with dantopaite is limited to its copper-poor variety, whereas in an elongate grain associated with lillianite, benjaminite exsolved into an intergrowth of benjaminite matrix and lamellae of a hitherto undescribed, copper-rich variety (Fig. 2d). These aggregates are fully analogous to the makovickyite – cupromakovickyite intergrowths (Topa & Paar 2008), pavonite – cupropavonite intergrowths (Karup-Møller & Makovicky 1979) and mummeite – cuprian mummeite intergrowths (Karup-Møller & Makovicky 1992).

In hand specimen, the mineral is greyish white in color, has a metallic luster and is opaque. It is brittle and has an uneven fracture. The mean VHN_{50}, determined on three identations on only one grain, is 190 kg/mm^2. This corresponds to Mohs hardness of 3½, very similar to that of other members of the PHS. The density of the natural material could not be measured because of the small size of the crystals, their scarcity and pervasive intergrowths with other phases. Using the empirical formula and Z = 1, the calculated density is 6.74 g/cm^3, thus very close to that of pavonite (6.75 g/cm^3), makovickyite (6.70 g/cm^3) and other members of the PHS.

In polished sections, in plane-polarized light, dantopaite is greyish white and lacks internal reflections. No reflection pleochroism can be discerned in the few grains available for this study. The bireflectance is perceptible in air and moderate in oil. Anisotropy is distinct in air and becomes enhanced in oil. Between crossed polars, bluish grey to brownish grey rotation-tints are common.

The reflectance data for dantopaite were obtained in air within the visible spectrum (400–700 nm) using a Leitz MPV–SP microscope-spectrophotometer. A WTiC reflectance standard (Zeiss 314) was used as a reference for the measurements. No measurements in oil were performed. The results are presented in Table 1. The R_{max} reflectance curve has a distinct maximum in the broad region of 450 nm, and the reflectance values decrease continuously toward 700 nm (Table 1). A corresponding maximum on the R_{min} curve and the decrease in reflectance toward 700 nm are barely perceptible. Still, the differences in reflectance on both curves are small, leading to a light grey colour of the mineral. In terms of reflectance and overall optical properties, there are only very minor differences between dantopaite and the other chemically closely related members of the PHS.

CHEMICAL DATA

Chemical analyses of dantopaite and associated phases were carried out in a polished section by means of an electron microprobe (JEOL JXA–8600 in WDS mode). The acceleration voltage was 25 kV, and the beam current, 30 nA; the correction procedure employed was on-line ZAF. Analytical results represent average of 37 analyses on two mineral grains. In Table 2, we give data for Cu, Ag, Pb, Bi, Te and S; no other elements with Z greater than 11 were detected. The empirical formula of dantopaite, based on (S + Te) = 22 atoms per formula unit, is $Cu_{1.06}Ag_{4.24}Pb_{0.90}Bi_{12.23}(Te_{0.11}S_{21.89})_{\Sigma 22}$. A simplified formula of this mineral is $Ag_5Bi_{13}S_{22}$. It requires Ag 13.61 wt.%, Bi 68.58 wt.%, and S 17.81 wt.%, in conformity with the theoretical composition of the N = 6 homologue of the pavonite series (Makovicky *et al.* 1977).

A small surplus of cations (~0.43 *apfu*) in the empirical formula, in comparison with the ideal formula, is due especially to the accumulation of Cu in the column of octahedra in the thinner structural slabs (see section on Crystal Structure), possibly supplemented by a partial replacement of Bi in some octahedral Bi sites.

Karup-Møller & Makovicky (1979) called the portion of copper *fitting into the ideal formula* together with silver (*i.e.*, occupying potentially the octahedral cation sites of the ideal structure) "*substitutional* ^{s}Cu", whereas the surplus copper they called "*interstitial* ^{i}Cu". For calculation of the order number N of the pavonite homologue analyzed by means of an electron microprobe, Karup-Møller & Makovicky (1979) proposed to normalize the atomic proportions according to the relation

$$Pb + Bi + Ag + {}^{s}Cu = 1$$

and to calculate the homologue order N applying the equation

$$N = [7 - 6Bi - 3(Pb + {}^{s}Cu)] / [2Bi + (Pb + {}^{s}Cu) - 1].$$

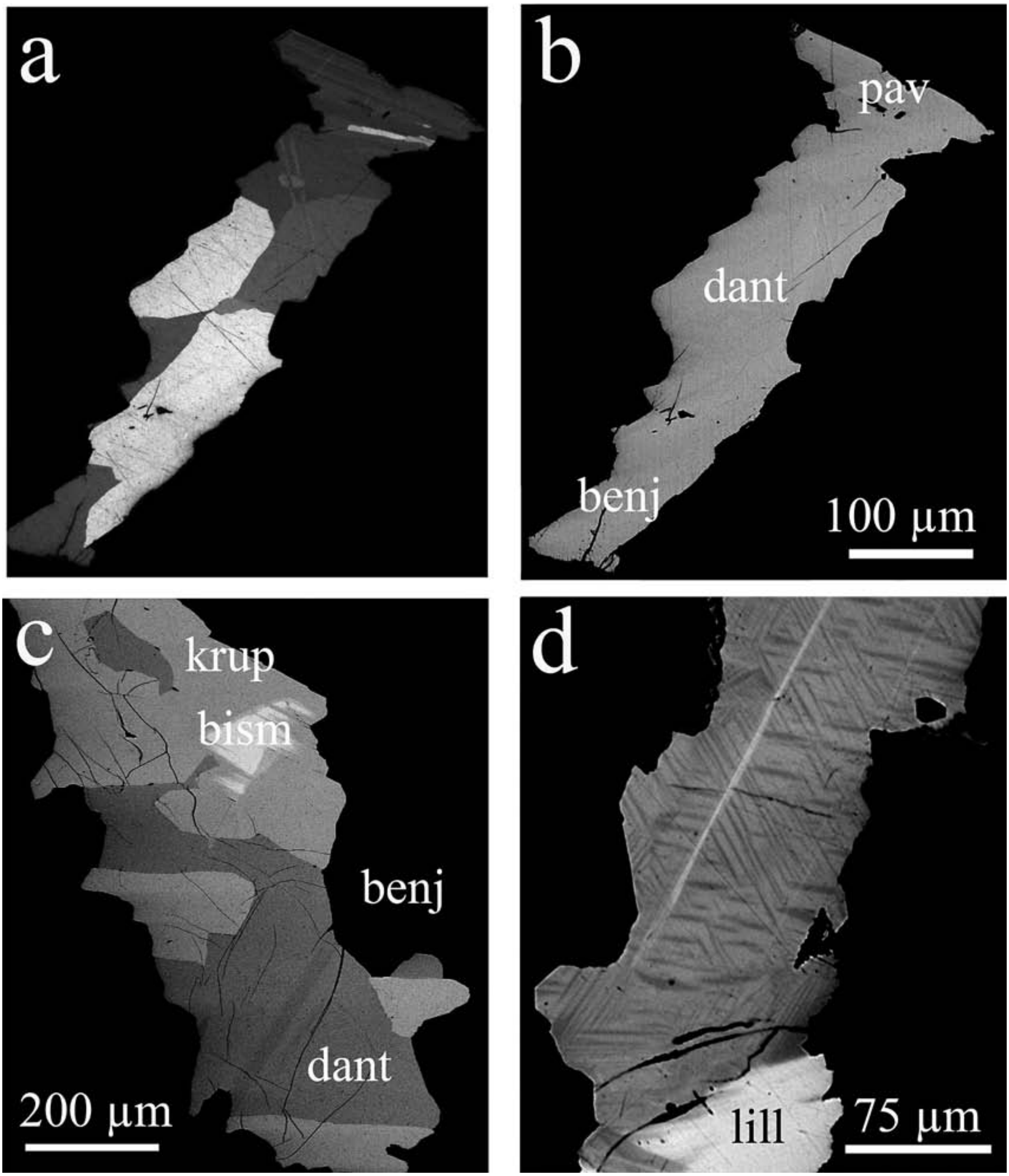

FIG. 2. The back-scattered electron images (b, c, d) and reflected-light photograph (a) of the dantopaite assemblage (a–b) and of the benjaminite exsolution pair (d). The mineral association, dantopaite (dant), pavonite (pav), benjaminite (benj), lillianite (lill), krupkaite (krup), and bismutinite (bism), is embedded in quartz.

It might be noted that Ag is involved in the latter expression indirectly, *via* the normalization procedure. It is impossible to distribute copper *a priori* between the ^{i}Cu and ^{s}Cu categories in a pavonite homologue with an unknown order-number N. Therefore, Karup-Møller & Makovicky (1979) proposed to use three compromise formulae to help bracket the right value of N: calculation of the value called N_{P1}, in which all copper is taken to be ^{i}Cu (*i.e.*, Cu is not considered in the normalization and is zero in the above equation), N_{P2}, in which all copper is considered ^{s}Cu (*i.e.*, all Cu is included in normalization and the equation), and N_{P3}, for which copper is distributed equally between interstitial and substitutional modes. Table 2 shows that the latter compromise gives the best results, closest to the integer values of N confirmed for dantopaite by structure determination.

In the formula $Cu_{1.06}Ag_{4.24}Pb_{0.90}Bi_{12.23}(S_{21.89} + Te_{0.11})_{\Sigma 22}$, 0.43 Cu *apfu* is "interstitial", whereas 0.63 Cu *apfu* is "substitutional". If we convert interstitial Cu plus the equivalent amount of Pb into Bi plus an interstitial vacancy ($^{i}Cu^{+} + Pb^{2+} \rightarrow \square + Bi^{3+}$), 0.90 Pb *apfu* reduces to 0.47 Pb *apfu*, whereas ^{i}Cu is eliminated. Redistributing this remaining Pb into ½ Ag + ½ Bi, and renaming ^{s}Cu as Ag, we obtain $Ag_{5.11}Bi_{12.90}S_{22}$, close to ideal $Ag_5Bi_{13}S_{22}$.

Figure 3 and Table 2 show that the closely associated pavonite, dantopaite and benjaminite from Erzwies are varieties with a moderate content of Cu and Pb and adopt approximately the same Ag : (Cu + Pb) ratio. This figure also shows the extent of Cu-for-Pb substitution in the exsolved, Cu–Pb-poor and Cu–Pb-rich components of the isolated benjaminite intergrowth described above.

For pavonite, $Cu_{0.87}Ag_{3.51}Pb_{0.72}Bi_{11.38}S_{19.93}Te_{0.07}$, ^{i}Cu is 0.49 atoms *apfu*. Subtraction of this and the equivalent amount of Pb leaves 0.23 Pb *apfu* to be converted into 0.11 Ag and 0.11 Bi. The resulting "substitution-free" composition $Ag_{4.01}Bi_{12.0}S_{20}$ is nearly the ideal formula of pavonite. The associated benjaminite, $Cu_{1.16}Ag_{5.03}Pb_{1.15}Bi_{13.16}S_{23.83}Te_{0.17}$, with ^{i}Cu equal to 0.50 atoms *apfu*, will have 0.65 Pb atoms *apfu* available for conversion into Ag + Bi, and the resulting "substitution-free formula" is $Ag_{6.02}Bi_{13.99}S_{24}$, again close to the ideal formula, $Ag_6Bi_{14}S_{24}$. The two products of exsolution in the isolated benjaminite pair have ^{s}Cu values equal to 0.40 and 0.91 atoms Cu *apfu*. The amount of interstitial copper exceeds the amount of Pb in the formula unit of the latter phase.

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

A fragment of dantopaite of irregular shape and measuring 0.05 × 0.07 × 0.09 mm was mounted on a Bruker AXS three-circle diffractometer equipped with a CCD area detector at the University of Salzburg. The crystal was separated from an acicular intergrowth of the sulfosalt species mentioned above. Similar to the other homologues of pavonite, dantopaite is monoclinic,

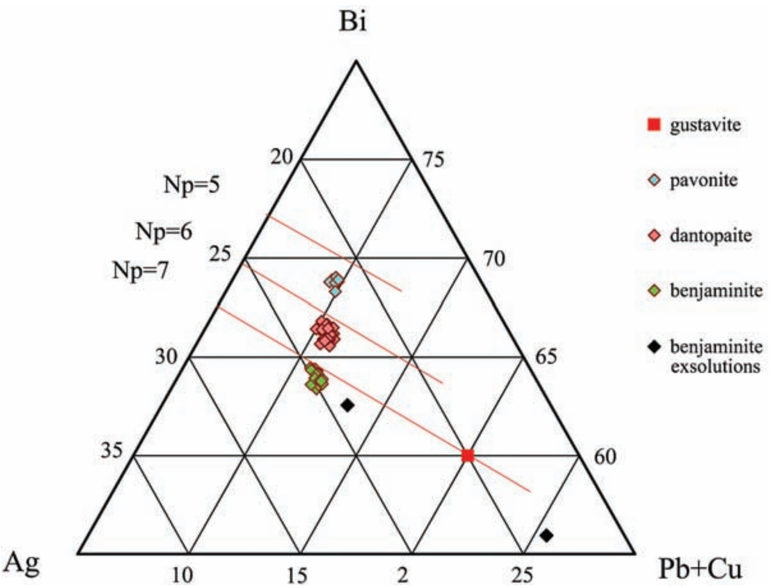

FIG. 3. Triangular diagram Ag – Bi – (Pb + Cu) showing the compositional data of the pavonite homologues from the Erzwies area plotted. N_p = 5, 6, and 7 denote pavonite, dantopaite and benjaminite, in this order. The data for the Cu–Pb-enriched benjaminite exsolution pair represent average results of the best analyses. Deviations of all three analyzed phases from the ideal composition lines (drawn in red) are due to the contents of "interstitial copper" in them (see text). Only the phases with no copper or with all copper of "substitutional type" will plot onto these lines. Ideal gustavite is a copper-free phase, whereas the substituted benjaminite is rich in copper, *i.e.*, the "overlap" observed is a product of projection from a quaternary system.

and the space group is $C2/m$. Cell dimensions are a 13.380(3), b 4.0492(9), c 18.690(4) Å, β 105.494(4)°, V 975.8(4) Å^3 and $Z = 1$ for $Ag_5Bi_{13}S_{22}$. The a:b:c ratio is 3.3044:1:4.6157 (from unit-cell parameters). Twinning was not observed.

Experimental details of data acquisition and crystal-structure determination are described in Table 3. We used the SMART system of programs for unit-cell determination and data collection, and SAINT+ for the calculation of integrated intensities and for the structure solution. From the systematic reflection conditions hkl: $h + k = 2n$; $h0l$: $h = 2n$; $0kl$: $k = 2n$; $hk0$: $h + k = 2n$; $0k0$: $k = 2n$; $h00$: $h = 2n$, the space group was found to be $C2/m$ (No. 12). The structure was solved by direct methods and refined with the SHELXTL package of programs (Bruker AXS, 1997). On the basis of interatomic distances, Bi, Ag, S and Cu were directly assigned in subsequent difference-Fourier maps. The final refinement was performed with anisotropic displacement parameters for all positions except those of copper. The final R_1 value is 7.3% ($F_o > 4\sigma$ [F_o]).

Refined positional and displacement parameters are listed in Table 4, selected interatomic distances in Table 5, and coordination-polyhedron characteristics calculated with IVTON program (Balić-Žunić & Vicković 1996) in Table 6. The crystal structure is illustrated in Figures 4, 5 and 6. A table of struc-

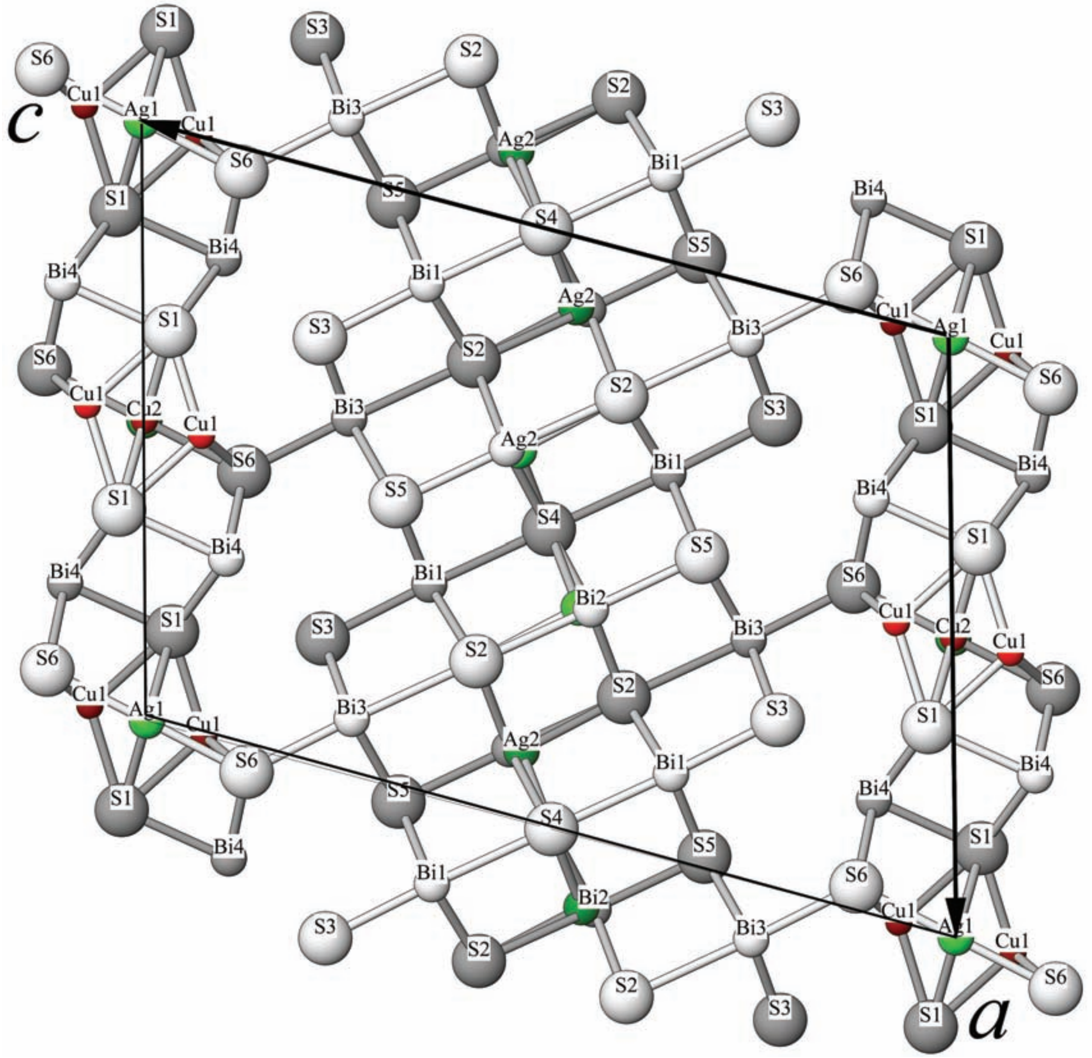

FIG. 4. Atom labeling in the unit cell of dantopaite. Atoms Ag1 and Cu2 are at different y levels; Bi2 and Ag2 substitute for one another at the same y level.

ture factors may be obtained from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Dantopaite CM48_467].

The crystal structure of dantopaite (Table 4, Figs. 4, 5 and 6) follows a structural scheme considered to be classical for pavonite homologues. The first one of the two alternating types of structural slabs is a thin one that contains a single column of edge-sharing octahedra. The latter are flanked and interconnected within the slab by double columns of Bi coordination pyramids. These thin slabs alternate with thick slabs composed of coordination octahedra of Bi and (Bi, Ag, Pb). The crystal-structure determination of dantopaite confirmed unambiguously its order number, N = 6, *i.e.*, there are six octahedra present in a diagonal row across the thicker slab (Fig. 6). With the *C*2/*m* space group, the structure contains three distinct coordination octahedra occupied by cations in the thick slab. A single site was refined as a mixed site, defined as (Bi2, Ag2) (Table 4). This is the most centrally located site in the thick slab (Fig. 6). The octahedral Bi1 site and the pyramidal Bi4 site in the thin slabs were found to be fully occupied by bismuth.

The marginal octahedra Bi1 and Bi3 are distinguished by typical short Bi–S bonds toward sulfur atoms, S3 and S6 respectively, situated on interslab surfaces. The Bi3 site has two additional short bonds (2.78 Å) to S3, whereas Bi1, sandwiched between Bi2 and Bi3, has four intermediate, almost equally long bonds, 2 × 2.84 Å and 2 × 2.85 Å, to S5 and S2, in that order (Table 5). On the basis of cation–anion distances observed, Pb is assumed to be concentrated at the Bi2 site, which flanks the central S4 atom in the thicker slab. According to the refinement, this site also hosts 0.18 Ag in a slightly asymmetric coordination (Ag2 in Fig. 4). Eccentricity of coordination octahedra in the thick slab (Table 6) increases progressively toward the more marginal Bi1, and further toward the protruding Bi3 position.

The Bi2–Ag2 octahedron in dantopaite is substantially larger than the analogous centrally located octahedron in the structure of substitution-free pavonite N = 5, which was refined as an Ag site (Makovicky *et al.* 1977). As already mentioned, the Bi2 octahedron is the site accumulating lead. The analogously positioned *Me*4 site in benjaminite (N = 7; Makovicky & Mumme 1979) was refined as 0.7 Ag and 0.3 Bi(Pb), again with interatomic distances somewhat shorter than those for Bi2 in dantopaite. In benjaminite, bismuth, with some Pb, is concentrated in the adjacent central *Me*3 site of the thicker slab.

The lone coordination-octahedron in the column of octahedra of the thin slab is foreshortened and skewed, with low sphericity (Table 6), analogous

TABLE 1. REFLECTANCE DATA (IN AIR) FOR DANTOPAITE FROM ERZWIES, GASTEINERTAL, PROVINCE OF SALZBURG, AUSTRIA

λ (nm)	R_{min}	R_{max}	λ (nm)	R_{min}	R_{max}	λ (nm)	R_{min}	R_{max}
400	41.2	46.8	520	41.2	48.0	620	40.2	46.6
420	41.4	47.5	540	41.0	47.3	640	39.8	45.8
440	41.8	48.9	**546**	**40.9**	**47.0**	**650**	**39.9**	**46.1**
460	41.6	48.6	560	40.9	47.3	660	39.9	45.8
470	**41.5**	**48.3**	580	40.5	47.1	680	39.6	45.4
480	41.6	48.5	**589**	**40.4**	**46.6**	700	39.6	45.2
500	41.4	48.1	600	40.4	46.8			

TABLE 2. AVERAGE RESULTS OF ELECTRON-MICROPROBE ANALYSES FOR DANTOPAITE AND ASSOCIATED MINERALS FROM ERZWIESS, GASTEINERTAL, AUSTRIA

no.	mineral	NA	Cu	Ag	Pb	Bi	Te	S	total	N_P	N_{P1}	N_{P2}	N_{P3}	ΣMe	ch	ev
1	pavonite	12	1.54	10.64	4.15	65.84	0.25	17.69	100.11	5	5.02	5.47	5.24	16.49	-0.13	-0.08
			0.04	0.09	0.05	0.09	0.05	0.07	0.16							
2	dantopaite	37	1.68	11.56	4.64	63.82	0.34	17.52	99.57	6	5.78	6.31	6.04	18.43	-0.20	-0.46
			0.06	0.12	0.14	0.18	0.08	0.07	0.28							
3	benjaminite	23	1.67	12.50	5.41	62.53	0.50	17.37	99.97	7	6.63	7.20	6.91	20.50	-0.03	-0.05
			0.06	0.09	0.14	0.24	0.08	0.06	0.26							
4	benjaminite	4	4.33	9.61	11.40	56.29	0.09	17.61	99.30	7	6.18	7.69	6.94	20.91	-1.45	-1.50
	dark lamellae		0.07	0.27	0.43	0.12	0.02	0.19	0.43							
5	benjaminite	5	1.69	12.08	7.24	60.76	0.11	17.49	99.40	7	6.81	7.40	7.11	20.40	-0.52	-0.54
	bright lamellae		0. 20	0.20	0.43	0.12	0.02	0.12	0.39							

1) $Cu_{0.87}Ag_{3.51}Pb_{0.72}Bi_{11.38}(Te_{0.07}S_{19.93})_{\Sigma 20}$
2) $Cu_{1.06}Ag_{4.24}Pb_{0.90}Bi_{12.23}(Te_{0.11}S_{21.89})_{\Sigma 22}$
3) $Cu_{1.16}Ag_{5.03}Pb_{1.15}Bi_{13.16}(Te_{0.17}S_{23.83})_{\Sigma 24}$
4) $Cu_{2.97}Ag_{3.89}Pb_{2.40}Bi_{11.65}(Te_{0.03}S_{23.97})_{\Sigma 24}$
5) $Cu_{1.17}Ag_{4.92}Pb_{1.54}Bi_{12.77}(Te_{0.04}S_{23.96})_{\Sigma 24}$

Empirical formulae were calculated on the basis of Te + S = n *apfu*; n = 20 for pavonite, n = 22 for dantopaite and n = 24 for benjaminite. The chemical homologue numbers N_{P1}, N_{P2} and N_{P3} were calculated after Karup-Møller & Makovicky (1979) (see text). The compositions are expressed in wt.%. NA: number of analyses. Standard deviation for the last digit is shown on the second line of each entry.

TABLE 3. SINGLE-CRYSTAL X-RAY DIFFRACTION: EXPERIMENTAL AND REFINEMENT DETAILS

Crystal data			
Chemical formula		$Cu_{1.06}Ag_{4.24}Pb_{0.90}Bi_{12.23}S_{22}$	
Chemical formula weight		3958	
Crystal system	Monoclinic	Space group	*C2/m*
a (Å)	13.380(3)		
b (Å)	4.0492(9)	D_x (mg m^{-3})	6.74
c (Å)	18.690(4)	No.of reflections for cell parameters	3008
β (°)	105.494(4)		
V (Å^3)	975.8(4)	μ (mm^{-1})	62.2
Z	1		
Crystal form	irregular	Crystal color	black
Crystal size (mm)	0.05 × 0.07 × 0.09		
Data collection			
T_{min}	0.068	T_{max}	0.129
No. of measured reflections	6350		
No. of independent reflections	1186		
No. of observed reflections	1051 for $F_o > 4σ(F_o)$		
Criterion for observed reflections	$I > 2σ(I)$		
R_{int}	11.87%		
$θ_{max}$ (°)	28.26		
Range of *h, k, l*	$-17 \le h \le 17$, $-5 \le k \le 5$ $-24 \le l \le 24$		
Refinement			
Refinement on F_o^2			
$R_1[F_o > 4σ(F_o)]$	7.41%		
$wR(F_o^2)$	16.76%		
S (GooF)	1.077		
No. of reflections used	1186		
No. of parameters refined	75		
Weighting scheme	$w = 1/[σ^2(F_o^2) + (0.0575P)^2 + 546P]$, where $P = (F_o^2 + 2F_c^2) / 3$		
$(Δ/σ)_{max}$	0.022		
$Δρ_{max}$ (e/Å^3)	8.22 [0.84 Å from Bi4]		
$Δρ_{min}$ (e/Å^3)	-6.51 [0.99 Å from Cu1]		
Extinction coefficient	0.00000(9)		
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)		

to the corresponding octahedra in the structures of pavonite homologues N = 4, 5, and 7 (Makovicky *et al.* 1977, Makovicky & Mumme 1979, Herbert & Mumme 1981, Mumme 1990, Topa *et al.* 2008). Only partial occupancy of this octahedral Ag1 site by 0.68 Ag is observed (Fig. 5). The coordination octahedron is flanked by partially occupied tetrahedrally coordinated copper Cu1 sites (each with 0.20 Cu), situated along the column, between two adjacent octahedra (Figs. 4, 5). In addition, about 0.08 Cu2 occupies flat-tetrahedral positions above and below Ag1 in the coordination octahedron itself (Fig. 5). Thus, in Figures 4 and 6, the nearly overlapping, mutually exclusive Cu2 and Ag1 sites actually are at two different *y* heights, although only approximately 0.6 Å apart. The Cu2 position corresponds closely to those observed in the pavonite N = 3 homologues $Cu_{1.57}Bi_{4.57}S_8$ (Tomeoka *et al.* 1980) and $Cu_{1.78}Bi_{4.73}Se_8$ (Makovicky *et al.* 2006).

Two "adjacent" Cu2 sites in the same coordination octahedron are mutually exclusive, situated at a distance of only 1.23 Å. The acceptable Cu2 neighbor is situated in the next coordination octahedron along the [010] direction, at a distance of 2.82 Å. In a similar manner, the Cu2–Cu1 distances are 1.93 Å (too close) and 2.95 Å, respectively. The Cu1–Ag1 distance is 2.42 Å; it can become a cation–cation contact common in the crystal chemistry of these elements only where these atoms deviate somewhat from their average position, extending this distance to a tolerable length. Both the Cu1 site and the silver site have the highest values of displacement factors of all cations (Table 4), whereas the displacement factor of Cu2 lies within the range seen for other cations in the structure of dantopaite. The bond-valence sum for Cu2 in Table 6 is influenced by the fact that the dimensions of the coordination polyhedron are in principle determined by the requirements of Ag1.

TABLE 4. POSITIONAL AND DISPLACEMENT PARAMETERS OF ATOMS IN DANTOPAITE

ATOM	*x*	*y*	*z*	*sof*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
Bi1	0.8543(1)	0	0.35128(8)	1	0.0185(4)	0.0160(6)	0.0172(7)	0.0219(8)	0.0044(5)
Bi2	0.6151(4)	0	0.4489(2)	0.82(2)	0.023(1)	0.027(1)	0.024(1)	0.020(2)	0.009(2)
Ag2	0.616(5)	0	0.464(3)	0.18(2)	0.023(1)	0.027(1)	0.024(1)	0.020(2)	0.009(2)
Bi3	0.0950(1)	0	0.25368(7)	1	0.0180(4)	0.0187(7)	0.0187(7)	0.0150(7)	0.0009(5)
Bi4	0.3066(1)	0	0.10002(8)	1	0.0243(5)	0.0318(8)	0.0253(8)	0.0181(8)	0.0105(6)
Ag1	0	0	0	0.69(9)	0.042(9)	0.049(6)	0.05(3)	0.040(5)	0.033(5)
Cu1	0.496(7)	0	0.071(5)	0.20(5)	0.115(38)				
Cu2	0	0.16(4)	0	0.08(9)	0.008(25)				
S1	0.6606(7)	0	0.0322(5)	1	0.013(2)	0.014(4)	0.015(4)	0.011(4)	0.006(3)
S2	0.2469(7)	0	0.4088(5)	1	0.020(2)	0.020(4)	0.021(4)	0.021(5)	0.011(4)
S3	0.7163(7)	0	0.2187(5)	1	0.014(2)	0.017(4)	0.011(4)	0.016(4)	0.010(3)
S4	0	0	0.5	1	0.030(3)	0.037(8)	0.022(7)	0.033(8)	0.016(7)
S5	0.4777(7)	0	0.3108(6)	1	0.023(2)	0.019(4)	0.014(4)	0.044(6)	0.020(4)
S6	0.9591(6)	0	0.1230(5)	1	0.016(2)	0.013(4)	0.017(4)	0.010(4)	-0.009(3)

U_{12} = 0 and U_{23} = 0 by symmetry; sof: site-occupancy factor.

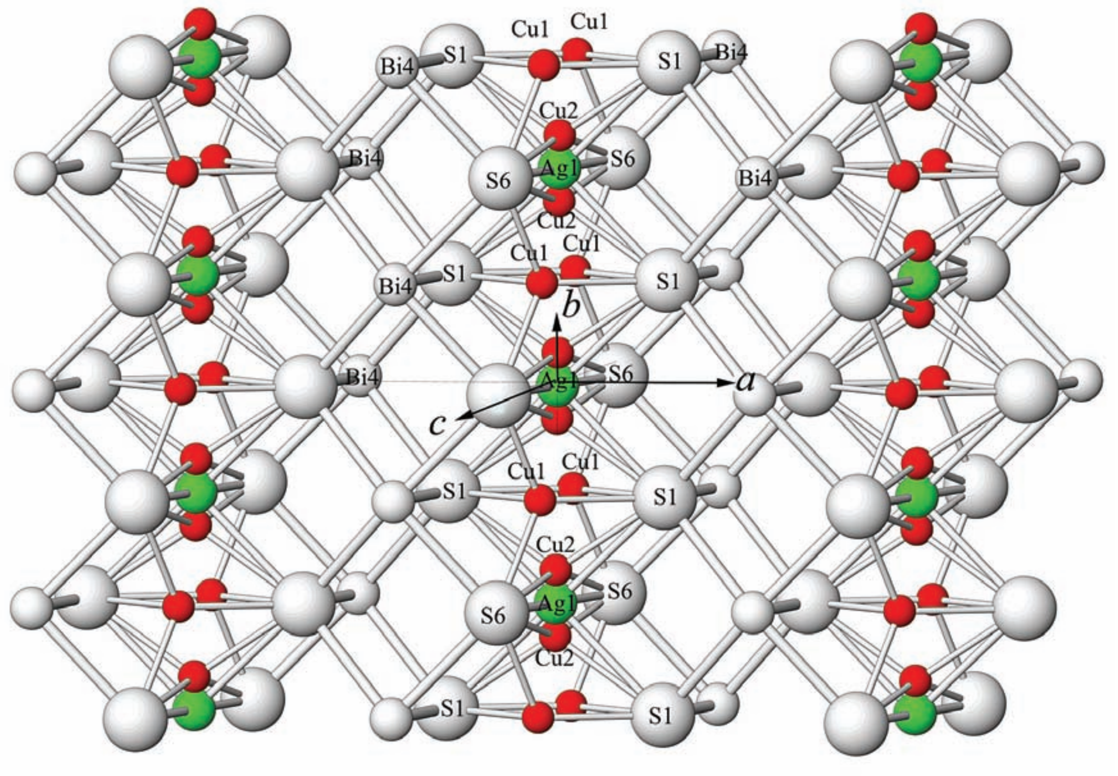

FIG. 5. Atom labeling for an oblique projection of the columns of octahedra occupied by silver and copper and the intervening columns of coordination pyramids of bismuth in the *thin layer* of the crystal structure of dantopaite.

TABLE 5. BOND DISTANCES (Å) IN POLYHEDRA IN DANTOPAITE

Bi1 –		Bi2 –		Bi3 –		Bi4 –	
S3	2.664(8)	S5	2.740(10)	S6	2.628(08)	S1	2.621(10)
S5	2.840(8) × 2	S2	2.803(9)	S3	2.779(06) × 2	S6	2.825(06) × 2
S2	2.854(8) × 2	S4	2.858(4) × 2	S5	2.932(08) × 2	S1	2.864(05) × 2
S4	2.938(1)	S2	2.911(8) × 2	S2	3.064(08)	S3	3.452(08) × 2
		S5	3.993(10)				
		Ag2 –					
		S2	2.586(52)				
		S4	2.742(48) × 2				
		S5	2.965(52)				
		S2	3.033(53) × 2				
Ag1 –		Cu1 –		Cu2 –			
S6	2.499(10) × 2	S6	2.354(53) × 2	S1	2.487(90) × 2		
S1	2.896(06) × 4	S1	2.439(81)	S6	2.582(42) × 2		
		S1	2.497(98)	S1	3.381(98) × 2		

The partially (~70%) occupied, linearly coordinated Ag1 site in the present structure has two short bonds, 2.50 Å; the remaining four bonds in the foreshortened octahedron are 2.90 Å. The partly occupied Ag2 position appears to represent silver, with the minimum cation–anion distance equal to 2.59 Å. This value, however, is influenced by the presence of Pb as well as the predominance of Bi in the "Bi2" coordination polyhedron, in which Ag2 is a minority site. The distances observed for Ag1 and Ag2 can be compared with a distance encountered for the linearly coordinated, fully occupied Ag site in neyite (2.416 Å; Makovicky *et al*. 2001).

Occupancy of a potential triangularly coordinated Cu position spanning the free, outwardly oriented wall of the Bi3 coordination octahedron has been checked, especially because of its analogy to the corresponding Cu positions in pure synthetic Cu–Bi pavonite homologues N = 3. This position in dantopaite would correspond to the Cu2 site in the marginal octahedra of the synthetic selenide $Cu_{1.78}Bi_{4.73}Se_8$ [the pavonite homologue N = 3] (Makovicky *et al*. 2006), with site occupancy equal to 0.03 Cu, and to the same site in $Cu_{1.57}Bi_{4.57}S_8$ [the synthetic sulfide homologue N = 3] with site occupancy equal to 0.12 (Tomeoka *et al*. 1980). Although traces of Cu or Ag persist at this location during the refinement process (up to 0.04 Cu per site combined with 0.97 Bi in the adjacent Bi3 site), these amounts are considered to lie below the error threshold of the current refinement, and the site was considered to be unoccupied. In makovickyite and cupromakovickyite, the marginal Bi2 polyhedra of the thick slab (Topa *et al*. 2008) resemble closely the Bi3 polyhedron in dantopaite. They were refined as a pure Bi site in both structures.

The reader should be attentive to the inferior quality of diffraction data that yield relatively high standard deviations of the occupancy values and of positional parameters for the Cu and Ag sites. Refinement results on the little-occupied copper and silver sites in the presence of an array of bismuth atoms will absorb the bulk of experimental errors. Furthermore, comparison with the results of the chemical analysis shows that the contents of heavy cations (Bi and Pb) are overestimated in relation to those of Ag. These problems probably are a reflection of the ubiquitous intimate intergrowths of two or several sulfosalts in practically each grain extracted, as also seen in the high value of R_{int}. Positional parameters of fully occupied sites are much less strongly influenced. Correlations between the displacement parameters of Ag1 and the occupancy of the adjacent Cu2 site, as well as the occupancy of the Ag1 site itself, reflect negatively upon the reliability of these values and result in high standard deviations.

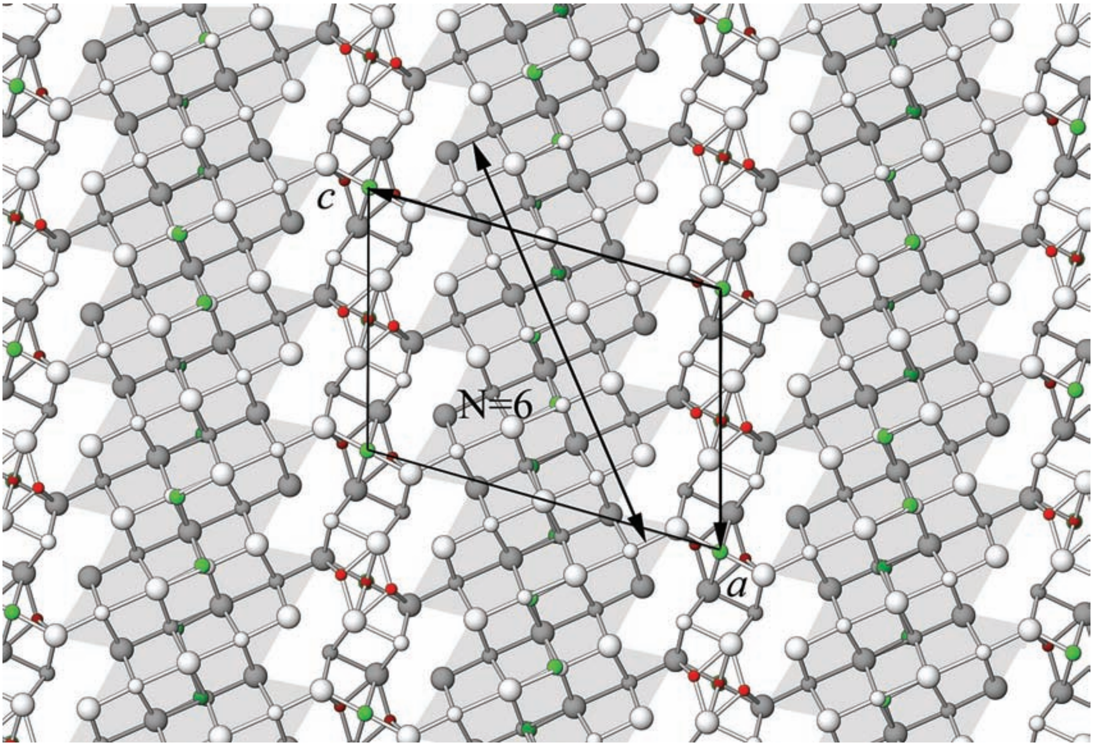

FIG. 6. The crystal structure of dantopaite projected along the *b* axis (~4 Å). A unit-cell is shown. In order of increasing size, circles represent Cu (red), Ag (green), Bi plus (Bi, Ag), and S positions. Void and filled circles represent atoms at two *y* levels, 2 Å apart. Thick slabs with rows of six Bi and (Bi, Ag) octahedra are shaded; thin layers are left unshaded.

The relatively large residual maximum close to the Bi4 site (Table 3) might reflect the presence of subsidiary ^{7}P lamellae in the diffracting dantopaite (^{6}P) material.

The sum of monovalent cations in the thin slab is 2.50 M^+ *apfu,* which amounts to 1.25 M^+ per octahedron of the thin slab. Comparison with chemical data shows that the bulk of excess cations is located here. The spatial distribution of the Ag1, Cu1 and Cu2 sites follows closely the usual pattern observed in the pavonite homologues, *e.g*., in makovickyite (Topa *et al.* 2008), which has 1.34 M^+ per octahedron of the thin slab. This justifies further the structure model presented.

The orientation of the short and long bonds in the marginal Bi3 coordination octahedron coincides with that observed in synthetic Cu–Bi pavonite homologues N=3, *i.e*., the shortest Bi–S bond bridges the gap between the two kinds of slabs and is oriented outward from the thicker slab. This agrees with conclusions by Makovicky *et al.* (2006), who suggested that the orientation of the short and long "horizontal" bond in this polyhedron is a function of the valence of the octahedrally coordinated cation in the thin slab. The short bond is oriented outward, as in the present case, where the coordination octahedra of the thin slab are occupied by monovalent cations, and inward, into the thicker slabs, where these octahedra are occupied by divalent cations.

As already mentioned, the cell parameters given were refined from single-crystal data. The amount of material was not sufficient for experimentally obtained X-ray powder data. A theoretical pattern (Table 7) was calculated with PowderCell 2.3 software (Kraus & Nolze 1999) in Debye–Scherrer configuration employing Cu Kα radiation (λ = 1.540598 Å), a fixed slit, and no anomalous dispersion. Cell parameters, space group, atom positions, site-occupancy factors and isotropic displacement factors from the crystal-structure determination were used.

TABLE 6. POLYHEDRON CHARACTERISTICS IN THE CRYSTAL STRUCTURE OF DANTOPAITE

1	2	3	4	5	6	7	8	9
Bi1	6	2.828	0.049	0.139	0.977	94.783	30.153	2.878
Bi2	6	2.846	0.018	0.053	0.939	96.592	30.688	2.727
Ag2	6	2.846	0.098	0.267	0.939	96.592	30.688	1.006
Bi3	6	2.849	0.086	0.237	0.998	96.827	30.800	2.849
Bi4	8	3.100	0.223	0.531	0.822	124.843	51.656	2.827
Ag1	6	2.764	0.000	0.000	0.778	88.442	27.388	1.311
Cu1	4	2.412	0.046	0.132	1.000	58.774	6.847	0.914
Cu2	4	2.555	0.047	0.134	1.000	69.844	6.847	0.652

The polyhedron characteristics used were defined in Balić-Žunić & Makovicky (1996) and Makovicky & Balić-Žunić (1998): 1) atom label, 2) coordination number, 3) radius r_s of a circumscribed sphere, least-squares-fitted to the coordination polyhedron, 4) "volume-based" distortion υ = [V(ideal polyhedron) – V(real polyhedron)] / V(ideal polyhedron). The ideal polyhedron has the same number of ligands. 5) "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. 6) "Volume-based" sphericity $SPH_V = 1 - 3\sigma_r r_s$; σ_r is a standard deviation of the radius r_s. 7) Volume of the circumscribed sphere, 8) volume of coordination polyhedron, 9) bond-valence sum (Brese & O'Keeffe 1991).

The Place of Dantopaite among Pavonite Homologues

Since its definition by Makovicky *et al.* (1977), the pavonite homologous series (PHS) of Ag–Cu–Pb–Bi sulfosalts became one of the most prolific homologous series, with an ever-increasing number of members. The

TABLE 7. CALCULATED X-RAY POWDER-DIFFRACTION DATA FOR DANTOPAITE

h k l	*d*, Å	*I* rel.	*h k l*	*d*, Å	*I* rel.
$\bar{2}$ 0 2	6.06	4	$\bar{4}$ 0 8	2.1324	3
0 0 3	6.00	3	$\bar{6}$ 0 5	2.1101	6
$\bar{2}$ 0 3	5.13	13	5 1 1	2.1037	14
2 0 3	3.904	11	3 1 5	2.1002	4
1 1 0	3.863	3	1 1 7	2.0665	7
0 0 5	3.602	4	0 2 0	2.0246	26
$\bar{2}$ 0 5	3.578	58	$\bar{6}$ 0 6	2.0215	15
1 1 2	3.452	90	$\bar{1}$ 1 8	2.0167	13
$\bar{1}$ 1 3	3.374	5	5 1 2	2.0133	25
$\bar{4}$ 0 1	3.331	37	0 0 9	2.0012	5
2 0 4	3.301	41	$\bar{5}$ 1 6	1.9868	9
4 0 0	3.223	11	6 0 2	1.9745	4
1 1 3	3.136	11	3 1 6	1.9334	6
$\bar{1}$ 1 4	3.055	8	$\bar{5}$ 1 7	1.8835	6
0 0 6	3.002	4	1 1 8	1.8808	4
$\bar{3}$ 1 1	2.9973	12	6 0 3	1.8709	3
$\bar{3}$ 1 2	2.9662	25	$\bar{1}$ 1 9	1.8381	4
3 1 0	2.9472	3	$\bar{3}$ 1 9	1.8176	4
$\bar{3}$ 1 3	2.8610	100	$\bar{4}$ 0 10	1.7889	4
2 0 5	2.8383	23	3 1 7	1.7832	5
3 1 1	2.8272	6	$\bar{5}$ 1 8	1.7771	6
$\bar{1}$ 1 5	2.7465	6	6 0 4	1.7648	3
$\bar{3}$ 1 4	2.7033	3	$\bar{2}$ 2 5	1.7620	14
3 1 2	2.6606	8	$\bar{4}$ 2 1	1.7301	10
$\bar{2}$ 0 7	2.6454	4	$\bar{7}$ 1 3	1.7273	8
2 0 6	2.4796	4	2 2 4	1.7258	10
3 1 3	2.4725	4	4 2 0	1.7145	4
$\bar{2}$ 0 8	2.3279	3	$\bar{7}$ 1 4	1.7134	4
1 1 6	2.2835	4	$\bar{4}$ 0 11	1.6484	3
$\bar{1}$ 1 7	2.2253	23	2 2 5	1.6482	8
5 1 0	2.1751	5	$\bar{8}$ 0 1	1.6448	8

TABLE 8. RELATIONSHIP TO KNOWN SPECIES

Mineral	pavonite	dantopaite	benjaminite
ideal formula	$Ag_4Bi_{12}S_{20}$	$Ag_5Bi_{13}S_{22}$	$Ag_6Bi_{14}S_{24}$
homologue number	5	6	7
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*m*	*C*2/*m*	*C*2/*m*
Cell parameters			
a (Å)	13.31	13.38	13.25
b (Å)	4.042	4.049	4.05
c (Å)	16.42	18.69	20.25
β (°)	94.02	105.494	103.14
Z (form. units/unit cell)	1	1	1
ρ_{calc} g/cm^3	6.75	6.74	6.81
R_1 factor (%)	11	7.3	11

original definition is based on the structure of pavonite (N = 5) (Makovicky *et al.* 1977) and on the structure of benjaminite refined somewhat later (N = 7) (Makovicky & Mumme 1979, Herbert & Mumme 1981) (Table 8); these minerals were originally defined by Nuffield (1954) and Shannon (1925) [modern definition by Nuffield (1953)], respectively. Subsequently, Karup-Møller & Makovicky (1979) found cupropavonite (N = 5) with a unit cell doubled compared to that of pavonite.

In 1992, Karup-Møller & Makovicky defined mummeite (N = 8) and Žák *et al.* (1994) described makovickyite (N = 4); their structures were resolved by Mumme (1990). Further refinement of the structure of makovickyite and description of the structure of a new phase with a doubled unit-cell, cupromakovickyite (defined by Topa & Paar 2008), was published by Topa *et al.* (2008). There exist naturally occurring lower members of the series, N = 3, with somewhat exotic compositions: grumiplucite, a Hg–Bi sulfosalt (Orlandi *et al.* 1998; structure by Mumme & Watts 1980), and kudriavite, a Cd sulfosalt (Chaplygin *et al.* 2005, structure by Balić-Žunić & Makovicky 2007).

The crystal structure of a synthetic, Cu–Bi, N = 3 member was determined first by Ohmasa & Nowacki (1973), then refined by Tomeoka *et al.* (1980); the corresponding Cu–Bi (N = 3) selenide was published by Makovicky *et al.* (2006). The synthetic N = 4 member is represented by a Cu–Bi sulfide as well (Ohmasa 1973), whereas synthetic Cd–Bi members have N values equal to 2 and 3, as do their regular intergrowths (Choe *et al.* 1997). The crystal structure of the synthetic N = 8 member, $Ag_{3.5}Bi_{7.5}S_{13}$, was described by Poudeu & Ruck (2005). A synthetic N = 4 selenide homologue combining In, Sn and Bi was described by Wang *et al.* (2009). The synthetic member N = 1, $MnSbSe_2I$ (Tougait *et al.* 2003), as well as the monoclinic form of $MnSbS_2Br$ (Doussier *et al.* 2006), represent an extension of the series to halogen sulfides. This approach proved very prolific as well, and a series of pavonite homologues with N = 1, 2, 3, 4, 5, and 7 was synthetized in the systems Ag–Bi–S–Cl *or* Br. For chlorine, N = 1 turned out to be a lillianite homologue. A conditional N = 0 member with a composition $AgBi_2S_2Cl_3$ was obtained as well (Poudeu & Ruck 2002, Poudeu *et al.* 2004, Ruck & Poudeu 2008a, b).

What has been conspicuously missing in this inventory, both among minerals and among synthetic compounds, and even in the series of recently synthetized halogen sulfides, is the sixth member of the pavonite homologous series. The only reference we know of describes a somewhat unusual N = 6 homologue, a synthetic selenide with Pb in interslab positions, synthetized and structurally analyzed by Mumme (1990). Unlike the latter compound, dantopaite is a "classical" pavonite homologue, close to the ideal composition $Ag_5Bi_{13}S_{22}$, with bismuth situated in the thin structural slabs.

NOTE ON THE FORMATION OF DANTOPAITE

According to the present state of knowledge, dantopaite is apparently a rare mineral. Its formation in the Erzwies deposit might be due to a rapidly and constantly changing composition of ore-forming solutions that resulted, in addition to the formation of complex aggregates of sulfosalts, in the simultaneous presence of three distinct pavonite homologues in the bunches of subparallel elongate sulfosalt crystals and in the same elongate composite grains. Another proof of this fluid regime are the corroded grains of ourayite in the decomposed PbS–$AgBiS_2$ aggregates and the presence of aggregates in which the composition of lillianite homologues varies along the vikingite–heyrovskyite line, similar to the "schirmerite" aggregates analyzed and described by Makovicky & Karup-Møller (1977).

EPILOGUE

Dantopaite is a new member of pavonite homologous series. As an answer to queries about the definition of a new mineral, raised by some members of the Commission for New Minerals, we should like to reiterate that members of a homologous series of accretionary type are independent chemical compounds, each with its own structure, unit cell, physical properties and chemical composition, as is the case of dantopaite relatively to pavonite and benjaminite (Table 8). They are *individual mineral species* (Makovicky 1989) and should be not confused with members of a solid-solution series. A distinct mineral (*i.e.*, a given structure) can even be a member of more than one homologous series, lying at the intersection of two series (*e.g.*, the pavonite homologous series and the proudite–felbertalite homologous series intersect in the structure of makovickyite). In cases of a complicated chemical composition, crystal-structure determination gives a final, unambiguous answer whether the mineral is a new species, as is in the present case.

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