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Description	The file attached is the Accepted/final draft post-refereeing version of the article.
Date Submitted	2017-03-30

1237R – revised version

The crystal structure of uytenbogaardtite, Ag_3AuS_2, and its relationships with gold and silver sulfides-selenides

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Abstract

The crystal structure of the mineral uytenbogaardtite, a rare silver-gold sulfide, was solved using intensity data collected on a crystal from the type locality, the Comstock lode, Storey County, Nevada (U.S.A.). The study revealed that the structure is trigonal, space group $R\bar{3}c$, with cell parameters: a = 13.6952(5), c = 17.0912(8) Å, and V = 2776.1(2) Å^3. The refinement of an anisotropic model led to an R index of 0.0140 for 1099 independent reflections. The structure consists of a sublattice of sulfur atoms forming a distorted body-centered cubic arrangement. The structure contains distinct tri-atomic linear groups (S–Au–S) and Ag atoms bonded to four S atoms (from four different linear groups) in a distorted tetrahedral arrangement. On the basis of information gained from this characterization, uytenbogaardtite is here definitively proved to be structurally different from petzite, Ag_3AuTe_2, and fischesserite, Ag_3AuSe_2. By means of high-quality single-crystal diffraction data, the

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DOI: 10.1180/minmag.2016.080.041

symmetry of the mineral was found to be trigonal, and not tetragonal as erroneously supposed. A revaluation of the powder diffraction data listed in the scientific literature for uytenbogaardtite according to the structural results obtained here leads to an excellent agreement. Crystal-chemical features of uytenbogaardtite, Au_2S, petrovskaite AgAuS, uytenbogaardtite–fischesserite series $Ag_3Au(S_{2-x}Se_x)$ and acanthite–naummanite series $Ag_2(S_{1-x}Se_x)$ are compared.

***Keywords*:** Crystal structure and symmetry; silver sulfides; gold sulfides; minerals; uytenbogaardtite.

Introduction

Uytenbogaardtite was defined as a new mineral species by Barton *et al.* (1978) during a study of the ores coming from three different regions: the Tambang Sawah, Benkoelen district, Sumatra (Indonesia), the Comstock lode, Storey County, Nevada (U.S.A.), and Zmeinigorsk, Altai, Russia. The mineral was found to form fine intergrowths with acanthite and electrum. An X-ray single-crystal study was not attempted by Barton *et al.* (1978) owing to the paucity of the mineral, and their structural study was limited to a low-quality X-ray powder investigation made difficult by the several coexisting phases in the selected material for the experiment. Barton *et al.* (1978) assigned a tetragonal cell of a = 9.76, c = 9.78 Å (Comstock lode), and a = 9.68, c = 9.81 Å (Tambang Sawah) to uytenbogaardtite, in relation with the studies done previously by Graf (1968) on the synthetic analogue.

Messien *et al.* (1966) reported the low-temperature Ag_3AuS_2 to be cubic, a = 9.72 Å, but Graf (1968) later argued that the symmetry is actually tetragonal. Observed reflections suggested a primitive space group with the only possible non-unit translational symmetry elements being 4_1- or a 4_3-axis (Graf, 1968). This author also pointed out that given the fact

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that not many 00*l* reflections were observed it is not possible to ascertain with confidence if a four-fold screw axis is present with the probable space group being either $P4_122$ or $P4_1$.

Recently, Seryotkin *et al.* (2011) solved the crystal structure of synthetic Ag_3AuS_2 and found that the compound is actually trigonal, space group $R\bar{3}c$. These authors compared the trigonal structure of Ag_3AuS_2 with that of cubic petzite (Ag_3AuTe_2) and fischesserite (Ag_3AuSe_2) and found that it cannot be attributed to the petzite group, because it exhibits a new structure type. By means of the synthesis and structural characterization of gold-silver sulfoselenides belonging to the $Ag_3Au(Se,S)_2$ series (i.e., $Ag_3AuSe_{1.5}S_{0.5}$, Ag_3AuSeS, and $Ag_3AuSe_{0.5}S_{1.5}$), Seryotkin *et al.* (2013a and references therein) proved the existence of two solid-solution series: petzite-type cubic Ag_3AuSe_2–Ag_3AuSeS (space group $I4_132$) and trigonal $Ag_3AuSe_{0.5}S_{1.5}$–Ag_3AuS_2 (space group $R\bar{3}c$). Both crystal structures differ in the distribution of Ag^+/Au^+ cations in distorted body-centered cubic sublattices of S/Se anions. The morphotropic transformation results from the shrinkage of anion packing accompanied by the shortening of Ag–Ag distances with increase of S content.

In the course of a research project dealing with the description and structural characterization of natural silver and gold chalcogenides (Bindi 2008, 2009; Bindi and Cipriani, 2004a, 2004b; Bindi and Pingitore, 2013; Bindi *et al.*, 2004, 2009, 2015), a fragment from the type locality (Comstock lode, Nevada) belonging to the mineralogical collections of the Natural History Museum of London (catalogue number E.1069, off BM 1983, 353) has been examined. Microscopic observations revealed that the sample consists of tiny uytenbogaardtite grains cut by veinlets of acanthite with gangue minerals of calcite and quartz.

To help resolve the concerns relating to the structure of uytenbogaardtite, new crystal structure data for the mineral from its type locality are presented here. We show that the

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78 structure of uytenbogaardtite mineral, earlier incorrectly interpreted as having a tetragonal
79 cell, is identical to that of the synthetic trigonal Ag_3AuS_2 end-member.

80

81 **X-ray crystallography**

82 A small crystal fragment (55 × 61 × 72 μm) was selected for the single-crystal X-ray
83 diffraction study. The intensity data collection (see Table 1 for details) was carried out by
84 means of an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (X-ray radiation
85 Mo*K*α, λ = 0.71073 Å) fitted with a Sapphire 2 CCD detector. A total of 714 frames of data
86 were collected at room temperature as 7 sets of omega runs with an exposure time of 80 s per
87 frame and a frame width of 1.00°. This afforded an overall data collection of 47568
88 reflections (1099 unique). The refined unit-cell parameters are a = 13.6952(5), c = 17.0912(8)
89 Å, and V = 2776.1(2) Å^3, which are in a very good agreement with those found by Seryotkin
90 *et al.* (2011) [a = 13.7104(4) Å, c = 17.1170(6) Å, and V = 2786.5(2) Å^3] for the synthetic
91 Ag_3AuS_2.

92 Data frames were processed using the *CrysAlis* software package (Oxford Diffraction,
93 2006) running on the Xcalibur 3 control PC. The program ABSPACK (Oxford Diffraction,
94 2006) was used for the absorption correction. The merging R for the data set decreased from
95 0.114 before the absorption correction to 0.032 after this correction. The observed reflection
96 conditions, together with the statistical tests on the distribution of $|E|$ values that strongly
97 indicated the presence of an inversion centre ($|E^2 - 1|$ = 0.957) and the indications from the
98 previous structure solution by Seryotkin *et al.* (2011), pointed unequivocally to the choice of
99 the space group $R\bar{3}c$. The structure solution was then initiated in this space group. The
100 positions of the atoms were determined by means of direct methods (Sheldrick, 2008). The
101 program SHELXL (Sheldrick, 2008) was used for the refinement of the structure. Neutral
102 scattering curves for Ag, Au and S were taken from the *International Tables for X-ray*

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Crystallography (Ibers and Hamilton, 1974). The occupancies of all sites were left free. They were found to be consistent with a full occupation by Ag, Au, and S, respectively, and then fixed. At the last stage, with anisotropic atomic displacement parameters for all atoms and no constraints, the residual value settled at $R = 0.0137$ for 907 observed reflections [$F_o > 4\sigma(F_o)$ level] and 38 parameters and at $R = 0.0140$ for all 1099 independent reflections. Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 1.81 and 1.78 $e^-/Å^3$, respectively. Experimental details and *R* indices are given in Table 1. Fractional atomic coordinates and anisotropic displacement parameters are reported in Table 2. Structure factors are deposited with the Principal Editor of Mineralogical Magazine at http://www.minersoc.org/pages/e_journals/dep_mat.html. Bond distances are reported in Table 3.

Optical properties

Qualitative observations of uytenbogaardtite in plane polarized reflected light are broadly in agreement with those of Barton *et al.* (1978). Under low power microscopic examination there is only a subtle difference between different orientations of uytenbogaardtite and the associated acanthite, both appearing a slightly bluish-grey against the dark grey gangue minerals calcite and quartz in association with pyrite (Fig. 1). However, observations using higher magnification objectives show that uytenbogaardtite is distinctly pleochroic in shades of slightly pinkish grey to slightly higher reflecting greenish grey against cross-cutting veins of acanthite (Fig. 2a). Moreover, at such higher magnification the mineral is distinctly light sensitive. For this reason, fully quantitative reflectance measurements were not made as the length of time taken to make measurements exceeded the period of relative stability prior to reaction and spotting of the uytenbogaardtite surface became obvious.

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It was observed during the light sensitivity reaction that orientations closer to R_o the basal section in uniaxial minerals, were more susceptible and hence more reactive presumably because electrons in the conduction band in this orientation are more easily excited by photons (Fig. 2b). In Figure 2 the slightly higher reflecting greenish grey orientation of uytenbogaardtite on the right of the image is close to R_o, while the slightly pinkish grey orientation is probably close to R_e. Since $R_o > R_e$ the mineral is uniaxial negative. In partially crossed polars, anisotropic rotation tints determined on the latter (Fig. 3) are from a pale green to deep purple.

Results and Discussion

Crystal structure of uytenbogaardtite

In the crystal structure of uytenbogaardtite, the Ag atoms are located in two crystallographically non-equivalent general positions. The four S atoms around each silver atom form an irregular tetrahedron. The Au atoms occupy also two crystallographically non-equivalent positions. Each of them is coordinated by two S atoms at a distance of 2.33–2.37 Å at an S–Au–S angle of ≈ 180°; in addition, each Au atom has six Ag atoms as its neighbors at a distance of 2.90–3.14 Å.

The structure may be described on the basis of infinite columns of edge-sharing $[AgS_4]$ sphenoids additionally connected by $[AuS_2]$ coordinations situated along threefold symmetry axes (Fig. 4). The crystal-chemical formula of uytenbogaardtite is $^{[4]}Ag_{12}(^{[2]}Au^{(7)}S_2)(^{[2n]}Au^{(7)}S_2)_3$ where the coordination number of a cation is enclosed in square brackets and that of an anion in parentheses. The building unit of the column, $Ag_{12}Au_4S_{20}$, consists of four S–Au–S linear groups (one of them lies on the column axis) and 2×6 Ag-tetrahedra (Fig. 4b). Multiplication of the building units by *c* symmetry plane forms the columns of uytenbogaardtite. The building units are joined in columns via six S^{2-} anions.

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Columns mutually joined by shared edges of Ag-tetrahedra are multiplied by base translations of rhombohedral lattice.

There are two types of S–Au–S complexes: strictly linear located along the column axis and slightly bent (indicated as "2n" (Lima-de-Faria *et al.*, 1990)) with the angle (S–$^{[2n]}$Au–S) of 179.35°. The complexes of the second type are located on the periphery of the columns.

The structure of the natural uytenbogaardtite is very similar to that of synthetic compound $Ag_{2.94}Au_{1.06}S_2$ (Seryotkin *et al.*, 2011), excluding the low-occupied Au3 site lacking in the structure of the current mineral sample. This disagreement is explained by the presence of AgAuS (petrovskaite) inclusion in the synthetic sample. A minor portion of this compound could affect the crystal data due to a topotactic integrowth of the two structures with similar anion sublattices (Seryotkin *et al.*, 2014).

Comparison with the crystal structures of Au- and Ag-sulfoselenides

Anion sublattice of many chalcogenides in this group is described according to the body-centered cubic packing (**bcc**) model. Such sublattice may be divided entirely into distorted tetrahedra or sphenoids (Bakakin, 2011; Seryotkin *et al.*, 2011). A part of sphenoids are occupied by Ag atoms; Au atoms are situated at the edges of vacant sphenoids. Thus, the structural features of a given compound are defined by the occupation of sphenoids by cations and by steric parameters of anions which form the sublattice.

The compounds with common formulae $(Ag,Au)_2(S,Se)$ are listed in Table 4. In these structures the sublattice of S- and Se-atoms forms a distorted (excluding Au_2S) body-centered cubic arrangement. It should be noticed that normalized volumes V_N (Bakakin and Seryotkin, 2009) are fairly close for the listed compounds (19.3–21.1 Å^3).

Worthy to note, the grade of distortion of anion sublattice does not relate directly to the symmetry of compound. The deviation from ideal **bcc** depends on deformation of its two-

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anionic subcell. Generally, the unit cell comprises several subcells, so the crystal symmetry depends on their combination. Coincidence of symmetries of anion sublattice and entire crystal structure was found only for Au_2S (Z = 2, Ishikawa *et al.*, 1995) and argentite, high temperature phase of Ag_2S (Z = 2, Cava *et al.*, 1980). In other related structures (Table 4) the unit cell comprises from 2 (acanthite, naumannite) to 24 (uytenbogaardtite) subcells in anion sublattice.

The compounds containing linear X–$^{[2]}$M–X groups in the structure have symmetry axis of third order. Silver chalcogenides without the linear groups are of lower symmetry. The meaningful example is cubic Au_2S which has only linear groups in the structure. Au^+ cations are located collinearly on body diagonals of anion **bcc** cells forming two interpenetrating three-dimensional networks with S^{2-} in tetrahedral coordination. The anion subsystem corresponds to ideal body-centered cubic packing.

Addition of cation with coordination number > 2 to linearly coordinated Au^+ results in the change of bonding system in the chalcogenide structure. Depending on the ratio of cations with different coordination, the three dimensional network of linear groups transforms to another configuration or breaks into fragments (chains, rings, single linear groups). For instance, in orthorhombic NaAuS with **bcc** anion packing the Na^+ cations in tetrahedral coordination are joined in a framework, and the $(^{[2n]}Au–S)^{\infty}$ chains coil in an unusual fashion so that they are interwoven to form layers reminiscent of "chicken-wire" (Axtell *et al.*, 1998).

Three fourths of Ag^+ cations form a tetrahedral framework in rhombohedral petrovskaite AgAuS. The linear groups S–(Au,Ag)–S form four interpenetrating three-dimensional networks (Seryotkin *et al.*, 2014). The number of Au cations alone is not enough to form the networks, so a fourth part of Ag^+ gained linear coordination. The detailed crystal-chemical formula of petrovskaite with cation ratio $^{[2]}M:^{[4]}M$ = 5:3 may be written as $^{[4]}Ag_6[^{[2]}Ag^{[2]}(Ag_{0.33}Au_{0.67})_3{}^{[2n]}Au_6{}^{(6)}S_6{}^{(4)}S_2]$, or simplified $^{[4]}Ag_3[^{[2]}Ag^{[2]}Au_4{}^{(6)}S_3{}^{(4)}S]$. The sublattice

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of sulfur anions has a strongly distorted **bcc** arrangement, caused by specific coordination of S^{2-}. Three fourths of anions are one-side coordinated by two Au^{+} and four Ag^{+}. The remaining part has only four neighboring Au^{+} forming a regular tetrahedron.

Uytenbogaardtite has a ratio $^{[2]}M:^{[4]}M = 1:3$ and its structure contains only isolated S–Au–S linear groups. In spite of the different coordination of cations, the deviation of anion sublattice from the **bcc** arrangement is quite small. All anions have similar coordination, which is likely to explain with the lower degree of distortion of anion sublattice compared to petrovskaite.

The structure of cubic fischesserite is composed of secondary building units of the same topology as in structure of uytenbogaardtite (Seryotkin *et al.*, 2011). The difference is in the manner of multiplication of building units in columns. In the uytenbogaardtite case, multiplication is realized by means of reflection and a translation shift by the *c* symmetry plane. In the fischesserite structure, they are multiplied by translation along the body diagonal without reflection. Both crystal structures differ in the distribution of Ag^{+}/Au^{+} cations. As a result, **bcc** sublattice of fischesserite is more distorted than that of uytenbogaardtite.

The structure of uytenbogaardtite tolerates the substitution of up to 40% of sulfur atoms by selenium. Two solid-solution Ag_3AuS_2–Ag_3AuSe_2 series exist: trigonal uytenbogaardtite-like Ag_3AuS_2–$Ag_3AuSe_{0.75}S_{1.25}$ and cubic fischesserite-like Ag_3AuSeS–Ag_3AuSe_2 (Seryotkin *et al.*, 2013a,b). The morphotropic transformation between the two structure types results from the shrinkage of anion packing accompanied by the shortening of Ag–Ag distances. It is generally assumed that the Ag–Ag interactions help to stabilize the structures of Ag–chalcogenides (Makovicky, 2006). However, the stabilizing effect of such interaction is limited to a certain range of interatomic distances, and an excessive shortening may cause instability of the crystal structure. For instance the S–S distances in the pseudocubic arrangement in uytenbogaardtite vary in the range 3.81–4.74 Å with a mean value of 4.22 Å,

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whereas the range observed in fischesserite is 3.43–5.20 Å, with a mean value of 4.33 Å. Since the Ag–Ag distance is equal to 2.89 Å in metal silver (Spreadborough and Christian, 1959), it can be assumed that the approach to this value is critical. Probably the same interaction causing destabilization of the fischesserite-like crystal structure causes the morphotropic transformation. Indeed, the shortest Ag–Ag bonds in Ag_3AuSSe and $Ag_3AuS_{1.5}Se_{0.5}$ are equal to 2.99 and 3.01 Å, respectively, whereas the calculated value for the model petzite-like structure of Ag_3AuS_2 is 2.93 Å (Seryotkin *et al.*, 2013a).

The morphotropic transition of the same nature may be found in another chalcogenide series between acanthite Ag_2S (Frueh, 1958) and naummanite Ag_2Se (Pingitore *et al.*, 1992; Seryotkin *et al.*, 2015). The compounds have distorted anion **bcc** arrangement with Ag^+ in planar ternary and distorted tetrahedral coordinations. Interestingly, the distortion of **bcc** arrangement is lower in monoclinic acanthite than in orthorhombic naumannite. There are short Ag–Ag distances ranging in the interval 2.9–3.0 Å in the structure of naumannite. Partial substitution of selenium by sulfur results in a further shortening of the distances (Seryotkin *et al.*, 2015). In the structure of acanthite Ag_2S the distribution of cations is slightly different and all Ag–Ag distances are ≥ 3.0 Å. This can be considered as a cause of morphotropic transition in this series.

Acknowledgements

X-ray intensity data were collected at CRIST, Centro di Cristallografia Strutturale, University of Florence, Italy. This work was funded by "Progetto d'Ateneo 2013" issued to LB. The paper benefited by the official reviews made by Tonči Balić-Žunić, Peter Leverett and Ernst Spiridonov.

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FIGURE CAPTIONS

Fig. 1. Reflected plane polarized light digital image in air illustrating subtle reflection pleochroism of uytenbogaardtite from slightly pinkish grey (left) to slightly greenish grey (right). Uytenbogaardtite is cut by veinlets of acanthite (slightly bluish grey) and the dark grey to black gangue minerals are calcite and quartz. A grain of pyrite gives useful visual reference towards the bottom of the image.

Fig. 2. Reflected plane polarized light digital image in air illustrating in more detail the relationships between uytenbogaardtite in different optical orientations and acanthite (a). The grain displaying slightly greenish grey rotation tints on the right of the image is starting to show spotting as a result of light sensitivity after about 30 seconds. (b) As for (a). After about 5 minutes exposure the spotting due to light sensitivity is more obvious particularly on the right hand grain and also at grain boundaries with acanthite.

Fig. 3. Reflected light digital image with partially crossed polars illustrating the anisotropic rotation tints in the grain on the left as pale green (a) to deep purple (b). The grain on the right approaches isotropy and is close to being a basal section, i.e. R_o.

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353 Fig. 4. The structure of uytenbogaardtite. Projection along *c*-axis (a). The $Ag_{12}Au_4S_{20}$
354 building units seen from the top and their joining into column along three-fold
355 symmetry axis seen from the side (b).

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TABLE 1. Data and experimental details for the selected uytenbogaardtite crystal

Crystal data	
Formula	Ag_3AuS_2
Crystal size (mm)	0.055 × 0.061 × 0.072
Form	block
Colour	black
Crystal system	Trigonal (hexagonal setting)
Space group	$R\bar{3}c$
a (Å)	13.6952(5)
c (Å)	17.0912(8)
V (Å^3)	2776.1(2)
Z	24
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	Mo$K\alpha$ (λ = 0.71073 Å)
Temperature (K)	293(2)
Detector to sample distance (cm)	6
Number of frames	714
Measuring time (s)	80
Maximum covered 2θ (°)	69.96
Absorption correction	multi-scan (*ABSPACK*; Oxford Diffraction 2006)
Collected reflections	47568
Unique reflections	1099
Reflections with $F_o > 4\,\sigma\,(F_o)$	907
R_{int}	0.032
Range of h, k, l	$-15 \le h \le 16$, $-18 \le k \le 18$, $-27 \le l \le 27$
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\,\sigma\,(F_o)$]	0.0137
Final R_1 (all data)	0.0140
Final wR (all data)	0.0321
Number of least squares parameters	38
Goodness of Fit	0.93
$\Delta\rho_{max}$ (e Å^{-3})	1.81
$\Delta\rho_{min}$ (e Å^{-3})	-1.78

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TABLE 2. Atoms, Wyckoff positions, atom coordinates and atomic displacement parameters ($Å^2$) for the selected uytenbogaardtite crystal

atom	Wyckoff	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}*/U_{eq}
Ag1	36*f*	0.04631(2)	0.21652(2)	0.33751(1)	0.0157(1)	0.0158(1)	0.01536(9)	0.00789(7)	0.00004(6)	0.00000(6)	0.01558(5)
Ag2	36*f*	0.83862(2)	0.04245(2)	0.42398(1)	0.0166(1)	0.0167(1)	0.0164(1)	0.00826(8)	-0.00017(6)	0.00002(6)	0.01658(5)
Au1	6*a*	0	0	0.25	0.01502(8)	0.01502(8)	0.0146(1)	0.00751(4)	0	0	0.01486(6)
Au2	18*e*	0.75437(1)	0	0.25	0.01646(7)	0.01648(8)	0.01603(6)	0.00824(4)	0.00001(2)	0.00002(4)	0.01632(5)
S1	12*c*	0	0	0.3887(1)	0.0217(4)	0.0217(4)	0.0245(6)	0.0108(2)	0	0	0.0226(3)
S2	36*f*	0.84379(8)	0.18078(7)	0.30325(5)	0.0241(4)	0.0244(4)	0.0243(4)	0.0122(3)	-0.0002(3)	0.0000(3)	0.0243(2)

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TABLE 3. Main interatomic distances (Å) for the selected uytenbogaardtite crystal

Ag1-S2^{i}	2.6301(9)	Au1-S1^{xii}	2.370(2)
Ag1-S2^{ii}	2.8207(9)	Au1-S1	2.370(2)
Ag1-S1	2.8423(6)	Au1-Ag1^{xiii}	3.0905(2)
Ag1-S2^{iii}	2.8795(9)	Au1-Ag1^{xii}	3.0905(2)
Ag1-Au2^{iv}	2.8998(3)	Au1-Ag1^{xiv}	3.0905(2)
Ag1-Au2^{v}	2.9595(2)	Au1-Ag1^{xv}	3.0905(2)
Ag1-Ag2^{v}	3.0062(3)	Au1-Ag1^{vi}	3.0905(2)
Ag1-Ag2^{i}	3.0294(3)	Au1-Au2^{v}	3.3640(2)
Ag1-Au1	3.0905(2)	Au1-Au2^{i}	3.3640(2)
Ag1-Ag1^{vi}	3.1865(5)	Au1-Au2^{xvi}	3.3640(2)
Ag1-Ag1^{vii}	3.2523(4)	Au2-S2^{xiii}	2.3294(9)
Ag2-S2^{viii}	2.546(1)	Au2-S2	2.3294(9)
Ag2-S1^{ix}	2.6215(5)	Au2-Ag1^{xvii}	2.8998(3)
Ag2-S2^{x}	2.6278(9)	Au2-Ag1^{xviii}	2.8999(3)
Ag2-S2	2.7780(9)	Au2-Ag1^{xix}	2.9595(2)
Ag2-Ag1^{xi}	3.0062(3)	Au2-Ag1^{xi}	2.9595(2)
Ag2-Ag1^{ix}	3.0294(3)	Au2-Ag2^{xiii}	3.1369(3)
Ag2-Ag2^{viii}	3.0821(4)	Au2-Au1^{ix}	3.3640(2)
Ag2-Au2	3.1369(3)		

Symmetry codes: (*i*) *x*-1, *y*, *z*; (*ii*) *x*-2/3, *x*-*y*-1/3, *z*+1/6; (*iii*) -*x*+1, -*x*+*y*+1, -*z*+1/2; (*iv*) *x*-*y*-2/3, *x*-1/3, -*z*+2/3; (*v*) -*x*+*y*+1, -*x*+1, *z*; (vi) -*x*, -*x*+*y*, -*z*+1/2; (*vii*) -*x*+1/3, -*y*+2/3, -*z*+2/3; (*viii*) *y*+2/3, *x*-2/3, -*z*+5/6; (*ix*) *x*+1, *y*, *z*; (*x*) -*x*+*y*+4/3, *y*-1/3, *z*+1/6; (*xi*) -*y*+1, *x*-*y*, *z*; (*xii*) *y*, *x*, -*z*+1/2; (*xiii*) *x*-*y*, -*y*, -*z*+1/2; (*xiv*) -*x*+*y*, -*x*, *z*; (*xv*) -*y*, *x*-*y*, *z*; (*xvi*) -*y*, *x*-*y*-1, *z*; (*xvii*) *y*+1/3, -*x*+*y*-1/3, -*z*+2/3; (*xviii*) *x*+2/3, *x*-*y*+1/3, *z*-1/6; (*xix*) -*x*+1, -*x*+*y*, -*z*+1/2.

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TABLE 4. Structural characteristics of silver and gold sulfides, sulfoselenides and selenides $(Ag,Au)_{2n}(S,Se)_n$.

Series	Compound (mineral)	Type	Unit-cell parameters (Å, degrees)				Space group, Z		V_N (Å^3)	Crystal-chemical formula	Reference
			a	*b*	*c*	*β*					
	Au_2S	**I**	5.0206	–	–		$Pn\bar{3}m$,	2	21.1	$^{[2]}Au_2{}^{(4)}S$	Ishikawa *et al.* (1995)
	AgAuS (petrovskaite)	**II**	13.4235	–	9.0873		$R\bar{3}m$,	24	19.7	$^{[4]}Ag_3[^{[2]}Ag^{[2]}Au_4{}^{(4)}S^{(6)}S_3]$	Seryotkin *et al.* (2014)
$Ag_{1.5}Au_{0.5}(S_{1-x}Se_x)$ $0 < x < 1$	Ag_3AuS_2 (uytenbogaardtite)	**III**	13.6952	–	17.0912		$R\bar{3}c$,	24	19.3		This work
			13.7104		17.1170				19.4	$^{[4]}Ag_3{}^{[2]}Au^{(7)}S_2$	Seryotkin *et al.* (2011)
	$Ag_3Au(S_{1.5}Se_{0.5})$	**III**	13.7752	–	17.2098		$R\bar{3}c$,	24	19.6	$^{[4]}Ag_3{}^{[2]}Au^{(7)}(S,Se)_2$	Seryotkin *et al.* (2013a)
	$Ag_3Au(S_{1.0}Se_{1.0})$	**IV**	9.8633	–	–		$I4_132$,	8	20.0	$^{[4]}Ag_3{}^{[2]}Au^{(7)}(S,Se)_2$	Seryotkin *et al.* (2013a)
	$Ag_3Au(S_{0.5}Se_{1.5})$	**IV**	9.9241	–	–		$I4_132$,	8	20.4	$^{[4]}Ag_3{}^{[2]}Au^{(7)}(S,Se)_2$	Seryotkin *et al.* (2013a)
	Ag_3AuSe_2 (fischesserite)	**IV**	9.965	–	–		$I4_132$,	8	20.6	$^{[4]}Ag_3{}^{[2]}Au^{(7)}Se_2$	Bindi and Cipriani (2004b)
$Ag_2(S_{1-x}Se_x)$ $0 < x < 1$	Ag_2S (acanthite)	**V**	4.23	6.91	7.87	99.58	$P2_1/n$,	4	18.9	$^{[3+1]}Ag^{[2+1]}Ag^{(5+2)}S$	Frueh (1958)
	$Ag_2(S_{0.5}Se_{0.5})$ (aguilarite)	**V**	4.2478	6.9432	8.0042	100.103	$P2_1/n$,	4	19.4	$^{[3+1]}Ag^{[2+1]}Ag^{(5+2)}(S,Se)$	Bindi and Pingitore (2013)
	$Ag_2(S_{0.25}Se_{0.75})$	**V**	4.2716	6.9707	8.1113	100.802	$P2_1/n$,	4	19.8	$^{[3+1]}Ag^{[2+1]}Ag^{(5+2)}(S,Se)$	Seryotkin *et al.* (2015)
	$Ag_2(S_{0.33}Se_{0.67})$	**VI**	4.2845	7.001	7.739		$P2_12_12_1$,	4	19.35	$^{[4]}Ag^{[3]}Ag^{(7)}(S,Se)$	Seryotkin *et al.* (2015)
	Ag_2Se (naumannite)	**VI**	4.3359	7.070	7.774		$P2_12_12_1$,	4	19.9	$^{[4]}Ag^{[3]}Ag^{(7)}Se$	Yu and Yun (2011)

Note. Isostructural compounds are shown by same Roman letters.

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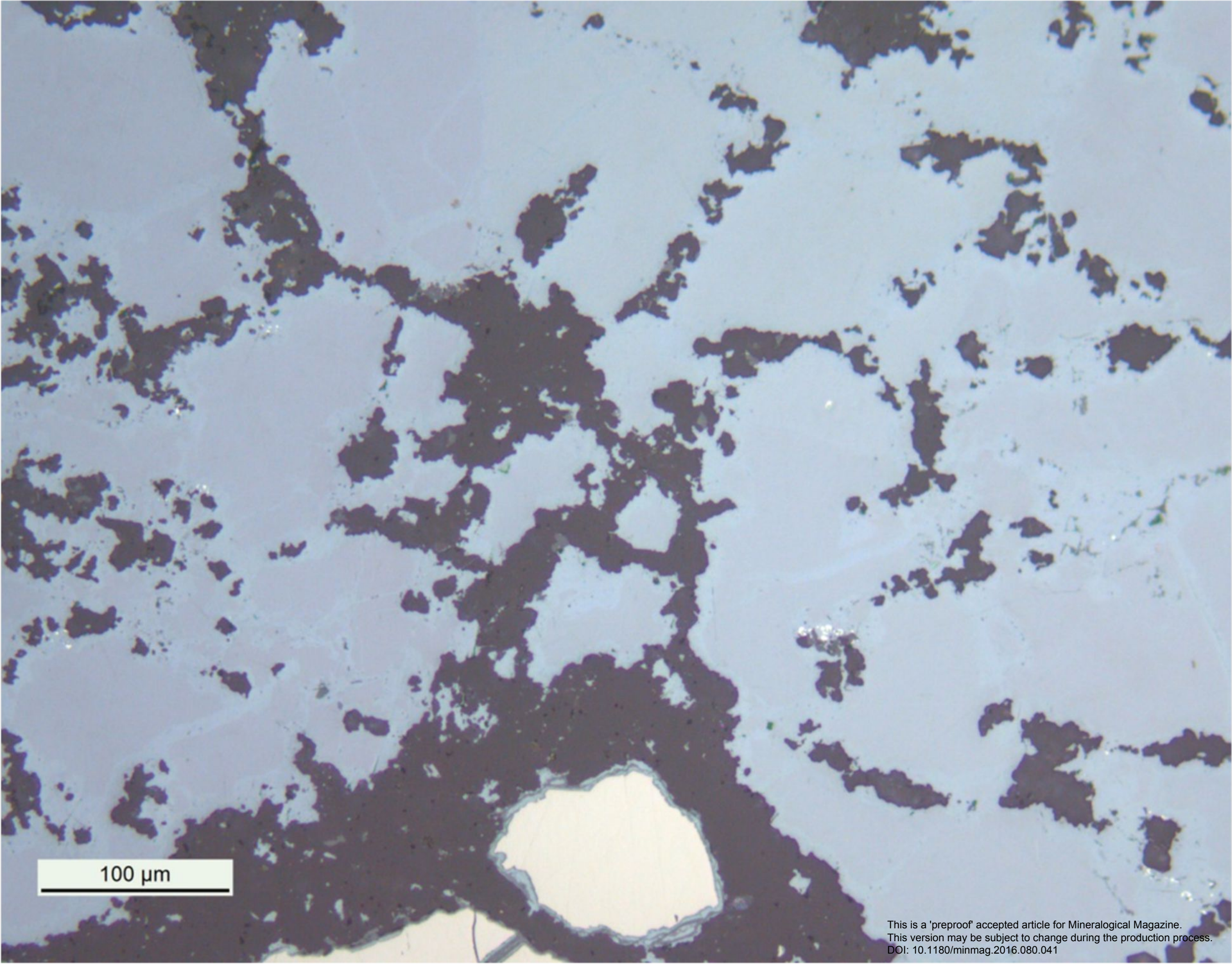

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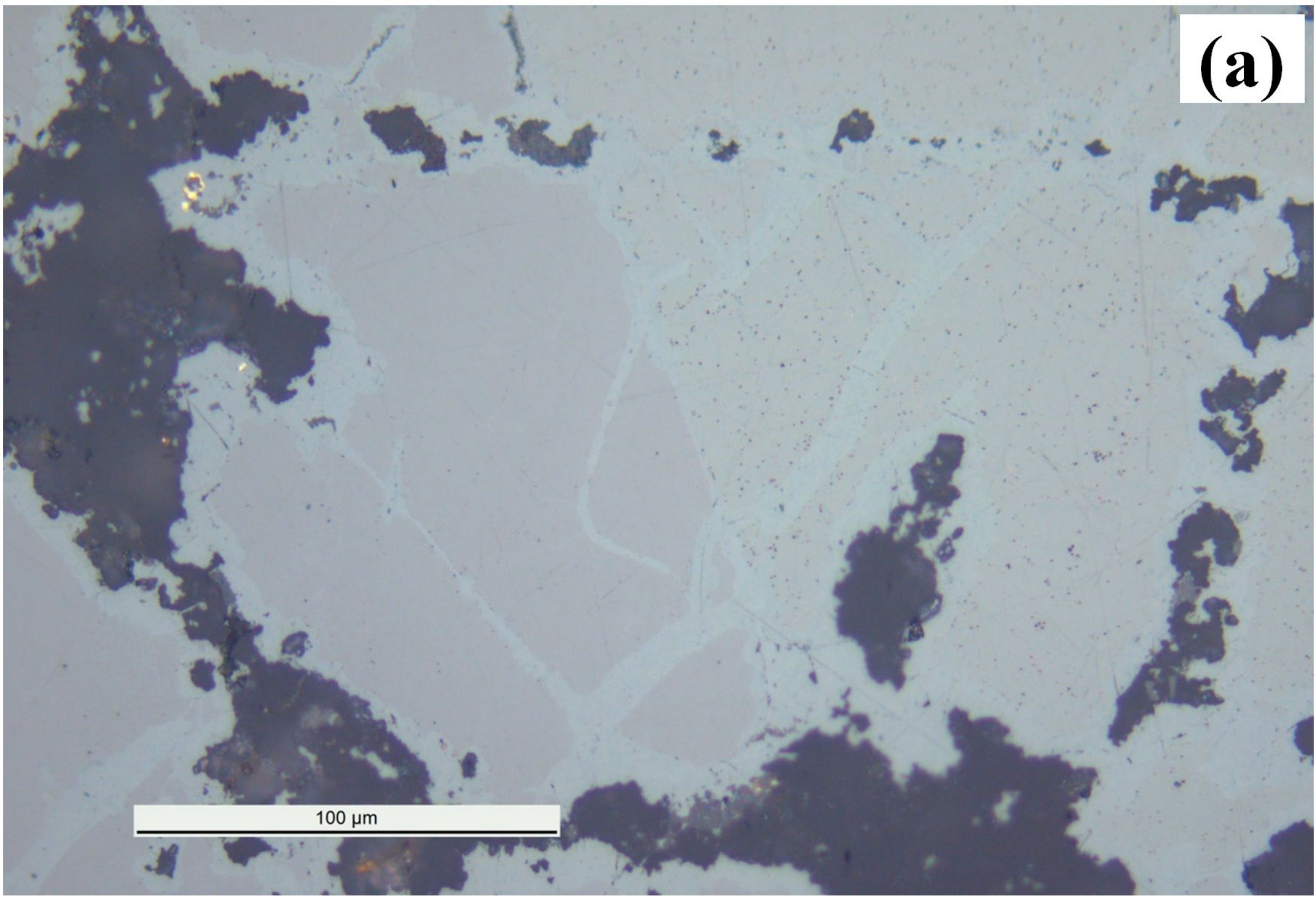

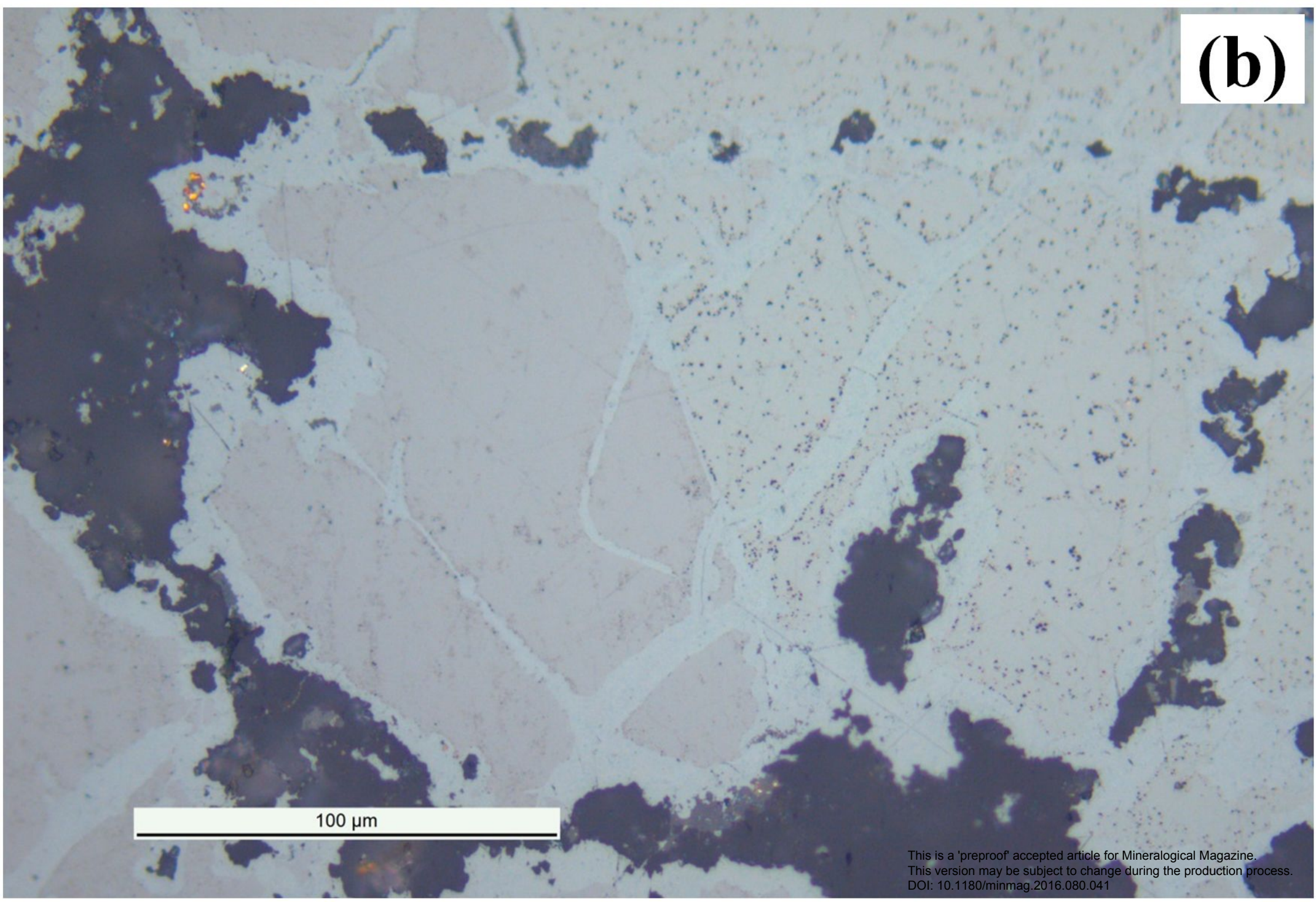

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(a)

100 µm

(b)

100 µm

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