

# Silver compounds as minerals in the eastern Karkonosze granitoid pluton, Sudetes, Poland

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## ABSTRACT:

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Twenty silver minerals of the sulphide, arsenide, selenide, telluride, sulphosalt and chloride groups were found in 13 locations in the Variscan Karkonosze granitoid pluton. Previously only one of these minerals was known from this area. The findings include species characterized in publications as rare or exceptionally rare, e.g., muthmannite and tsnigiite. They occur in pegmatites and quartz veins; their parageneses are described. The studies include determination of chemical compositions, formulae calculations and recording of XRD patterns. Inclusion studies in paragenetic quartz indicate that they crystallized from epithermal fluids with a common but low component of CO<sub>2</sub>. The results suggest that the minerals formed from trace elements (Ag included) in the Karkonosze granitoid due to very local degrees of recrystallization of the host granitoid.

**Key words:** Silver; Sulphide; Arsenide; Selenide; Telluride; Chloride; Fluid inclusions; Karkonosze granitoid.

## INTRODUCTION

Silver minerals in the Lower Silesian part of the Bohemian Massif accessible to direct geological research and to mining have been found and exploited at many localities. Probably the earliest publication on silver minerals from Silesia and Erzgebirge was by Agricola (1530, pp. 131–132, *argentum rude, filber ertz*). It included acanthite (*argentum rude plumbei coloris, glafz ertz*), a mineral of the tetrahedrite group (*argentum rude nigrum, schuuratz ertz*), another Ag mineral of this group (*argentum rude cineraceum, grau ertz*), proustite (*argentum rude puniceum, rot gulden ertz*), pyrargyrite or proustite (*argentum rude ruffum, rotbrendigertz*) and chlorargyrite (*argentum rude purpureum, brun ertz*). Later, data on silver mineral occurrences in the Silesian area were collected by Fiedler (1863), Traube (1888), next by Lis and Sylwestrzak (1986)

and by Sachanbiński (2005) (cf. references cited in the listed publications). These publications described the locations of silver mineral occurrences and silver ore exploitation in the Silesian part of the Bohemian Massif. However, in the Polish part of the Karkonosze pluton, which is a component of this massif, the first credible information on the finding of a tiny native silver flake in pegmatite was published by Gajda (1960). A second occurrence of native silver was described by Kozłowski and Sachanbiński (2007). Recently, matildite was also found (Łukasz Karwowski, pers. comm., 2021). Further studies by the present authors resulted in the finding of 22 localities with microspecimens of native silver in the Karkonosze pluton; they are elaborated separately. This article shows the characteristics of 20 minerals – silver compounds (sulphides, sulfosalts, selenides, tellurides, arsenide and chloride) from this pluton.



Text-fig. 1. Eastern part of the Karkonosze Variscan granitoid pluton and its metamorphic envelope: 1 – porphyritic monzogranite and granodiorite; 2 – medium-grained biotite monzogranite; 3 – fine-grained monzogranite; 4 – hornfels; 5 – gneiss; 6 – chlorite-mica schists; 7 – mafic metamagmatites and schists; 8 – mainly mafic metamagmatic rocks; 9 – faults; 10 – sampling localities of the silver minerals. Geological background after Krenz *et al.* (2001), changed. Insert – location in Poland.

## GEOLOGICAL SETTING

The Karkonosze Variscan granitoid batholith is c. 70 km W-E long and from 8 to 20 km N-S wide. Its rocks were first recognized as granite by Pallas (1778). Gerhard (1781, p. 47) published a more precise description and characterized its gneiss envelope. Rose (1842) indicated varieties of the Karkonosze granitoids: porphyritic one (several-centimetre long orthoclase porphyrocrysts in fine-grained quartz-feldspar-mica groundmass), equigranular medium-grained one with typical granitoid composition and very fine-grained rock with albite as the main feldspar (aplite). Comprehensive petrographic details were given by Klockmann (1882a, b). Later, ‘Ganggranit’, i.e., granitoid pegmatites were described (Müller 1889). Subsequently, petrographic data on the Karkonosze batholith were collected by Berg (1923). Thorough studies of the Karkonosze granitoids (Borkowska 1966) also resulted in a recognition of their varieties: central granite (approximately earlier porphyritic granite), ridge granite (equigranular one) and granophyric granite (fine grained one); in the QAPF system (Le Maître *et al.* 2002), the so-called central and crest granite are monzogranite and granodiorite (in various parts of the central or crest ones),

whereas the granophyric kind is monzogranite only (Text-fig. 1; cf. Krenz *et al.* 2001). Good general descriptions of tectonic, petrographic, geochemical, and other aspects were published by Chaloupský *et al.* (1989) and Klomínský (2018). The Karkonosze granitoid formed at 990 to 840°C from a melt of tonalitic to granitic composition (Kozłowski 2007), as indicated by studies of melt inclusions in magmatic quartz. The intrusion was recognized as polyphase (Cloos 1924; Žák and Klomínský 2007; Žák *et al.* 2013, 2014; Klomínský 2018) with possible episodes of felsic and mafic magma mixing or mingling (Słaby and Martin 2008). The batholith formed in the late Carboniferous, c. 312–315 Ma ago (Žák *et al.* 2013; Kryza *et al.* 2014a, b; Mikulski *et al.* 2020).

This pluton is a part of the Lower Silesian NE domain included into the Variscan Bohemian Massif (Mazur *et al.* 2018). The domain was composed of Neoproterozoic fragments of the Gondwana continent, i.e., Lower Palaeozoic granitoids metamorphosed to gneisses, Middle Palaeozoic sediments accumulated on continental margins, ophiolite series, Carboniferous granitoids, and rocks of intramontane basins (Mazur *et al.* 2007). The accretion, collision of crustal fragments, pluton formation and related faults of various size formed until the Alpine orog-

eny, resulting in a blocky distribution of the rocks in Lower Silesia (Quenardel *et al.* 1988; Mazur *et al.* 2010). The Karkonosze pluton belongs to this pattern. It has an envelope of metamorphic rocks (Text-fig. 1): on the northern edge lower Palaeozoic gneiss, mica-chlorite and amphibolite schists with hornfels, and metamafites with limestone; similar rocks form the eastern and southern exocontact area but with local high-pressure (up to 10 kbar) schists (Oberc 1961; Teisseyre 1971; Borkowska *et al.* 1980; Chaloupský *et al.* 1989; Mazur 2003, 2005; Żelaźniewicz *et al.* 2003; Mazur *et al.* 2007, 2010, 2018 and references therein).

## OUTCROPS STUDIED

The investigated specimens of silver minerals were found in samples taken from pegmatites and quartz veins in the eastern part of the Karkonosze pluton in the years 1969–2000. Pegmatites in the Karkonosze granitoids (usually in the porphyritic type) are commonly several tens of centimetres in size; only exceptionally they attain several meters. Potassium feldspar, quartz, oligoclase, albite, biotite and muscovite are their main components, arranged in concentric zones, usually with a central miarole in approximately isometric pegmatites or in roughly parallel bands in the lenticular or vein-type varieties. Accessory minerals may occur in the central parts, but are also dispersed in the whole pegmatite (Matyszczyk 2018).

The common opinion on the origin of pegmatites in granitoids is that they formed as late stage magmatic bodies (see e.g., Fersman 1940, pp. 23–32; London 1992; Thomas *et al.* 2006; Simmons 2008). However, Schaller (1925, 1926) concluded that they may appear due to accumulative metasomatic recrystallization of the parent aplite or granite. Features indicating recrystallization for the origin of pegmatites have also been found in the Karkonosze pluton (Kozłowski 1978, 2002a). Formally, the niobium–yttrium–fluorine (NYF) family *sensu* Černý and Ercit (2005, see also Černý *et al.* 2012) is generally accepted as the classification unit for the pegmatites of this pluton (Pieczka *et al.* 2015; Evans *et al.* 2018; Matyszczyk 2018). An exact list of minerals found in the pegmatites was published by Pieczka *et al.* (2019).

Quartz veins in the Karkonosze pluton (Kozłowski 1973, 1978 and references therein) are not rare. Their thickness and extension are very variable. Though most commonly completely filled by quartz (various shades of grey, almost transparent or milky, rarely by amethyst), in some places they contain small voids

with subhedral crystals. In a number of veins feldspars, micas, chlorite, sulfides, hematite, etc. may be found as minor components. The veins are almost vertical, approximately horizontal and, distinctly more rarely, inclined.

The occurrences of the investigated silver minerals (Text-fig. 1) are described below.

**Cicha Równia Mt.** (15°24.82'E, 50°49.67'N): northern slope, c. 0.5 km toward Rozdroże pod Cichą Równią, near Jelenia Meadow. Small rock of the porphyritic granitoid up to 1.8 m high with a vertical veinlet of grey quartz, c. 4 cm thick with 1–2 cm voids containing single grains of pyrite, arsenopyrite, hematite, goethite and rarely chlorargyrite on the latter.

**Granicznik Mt.** (15°22.47'E, 50°48.98'N): a quartz vein (4–7 cm thick), dipping to the south and located c. 50 m westwards from the summit in a porphyritic granitoid, contained accessory calcite, native arsenic, native silver, chalcocite, pyrite, chalcopyrite, arsenopyrite, stromeyerite and novákite.

**Kowarska Czuba Mt.** (15°52.22'E, 50°47.33'N): an outcrop on the western slope of the mount, c. 250 m from the summit, located south of an abandoned porphyritic granitoid quarry; a 12–14 cm thick horizontal quartz vein contained dispersed grains of pyrite, chalcopyrite, arsenopyrite and löllingite; crystals of proustite and muthmannite were found in a fissure.

**Krowia Kopa Mt.** (15°20.11'E, 50°52.03'N): an almost horizontal platy outcrop of porphyritic granitoid, located c. 300 m to the west of the mount summit, near the contact with the Izera gneiss. A pegmatite nest, c. 30 cm in diameter, in the central part contained accessory zeolites, calcite, fluorite, pyrite, sphalerite and chalcopyrite. One chalcopyrite crystal included minute grains of balkanite; in the same nest pyrargyrite grains were partly overgrown by rock crystal.

**Michalowice** (15°34.50'E, 50°50.25'N): quarry of porphyritic granitoid, now abandoned. Pegmatite in the western wall of the excavation with accessory epidote, chlorite, pyrite, chalcopyrite, stibnite and galena also contained acanthite and owyheelite.

**Miedziane Skaly Mt.** (15°55.57'E, 50°51.08'N): block of porphyritic granitoid, c. 130 m to the north-west of the mount summit with vertical grey quartz veinlet, 4–6 cm thick, containing grains of pyrite, chalcopyrite, tetrahedrite group minerals, galena, acanthite, aguilarite, naumannite and stromeyerite;

**Piaskowa Mt.** in Hutniczy Ridge (15°56.03'E, 50°51.84'N): equigranular granitoid in the escarpment of a path, c. 300 m west of the mount summit.

Horizontal quartz vein with rare feldspar and calcite crystals contained dispersed grains of pyrite, chalcopyrite, acanthite and stromeyerite; close to galena and pyrite a grain of tsnigriite was found.

**Popiel Mt.** (15°56.27'E, 50°53.28'N): southern slope, half of the distance between the mount summit and Bóbr river. Almost vertical grey quartz veinlet, 10–12 cm thick, with dispersed grains of calcite, pyrite, galena, chalcopyrite and tetrahedrite group minerals, moreover cervelleite and stützite grains were found.

**Ptak Hill** (15°36.41'E, 50°51.90'N): a block of porphyritic granitoid in a small landslide on the southern slope near the summit. Pyrite, chalcopyrite, galena, bismuthinite and matildite were found in a 2–3 cm thick veinlet of grey quartz.

**Rybień Mt.** (15°49.63'E, 50°54.92'N): rocks of porphyritic granitoid, c. 400 m to the south of the summit towards Maciejowa village. A grey quartz vein, 15–18 cm thick, contained minute rock crystals, calcite, violet fluorite, pyrite and acanthite in voids up to 1 cm in size.

**Splawna Hill** (15°27.45'E, 50°49.91'N): abandoned quarry of porphyritic granitoid in the eastern slope of the hill, left bank of the Czerwony Creek near its estuary to Kamienna River. In the NW wall of the pit, a 2–3 cm thick quartz veinlet was found with dispersed grains of native bismuth, pyrite, chalcopyrite, molybdenite, acanthite, argyrodite, canfieldite and cassiterite.

**Szklarska Poręba Huta** (15°29.60'E, 50°49.62'N): a c. 2 cm thick quartz veinlet occurred in the NW wall of a quarry in granophyric granite. In small voids it contained bismuthinite, volynskite and acanthite paramorph after argentite.

**Wolek Mt.** (15°56.22'E, 50°50.28'N); c. 120 m to the northwest from the mount summit a 10–14 cm thick quartz-feldspar veinlet in a bulge of fine-grained granitoid contained rare small grains of pyrite, chalcopyrite, galena and freieslebenite.

## INVESTIGATION METHODS

Specimens were examined under a binocular microscope to separate minerals for further investigation. Preparations glued on glass, polished and covered by carbon film were made from the selected minerals. Afterwards they were checked for the presence of silver and next analysed quantitatively by WDS electron probe microanalysis with Cameca SX100 and ARL SEMQ analysers. The analysis conditions were as follows: electron beam

accelerating voltage 7–20 keV, beam current 8–12 nA, diameter of beam spot 3–10  $\mu\text{m}$ , count time 4–15 sec. Some preparations were frozen by liquid nitrogen during analysis. These X-ray peaks were used for quantitative analyses: *AgLa*, *AsLa*, *AuLa*, *BiMa*, *BrKa*, *CdKa*, *ClKa*, *CoKa*, *CuKa*, *FeKa*, *GeKa*, *HgMa*, *IKa*, *NiKa*, *PbM $\beta$* , *SKa*, *SbLa*, *SeLa*, *SnKa*, *TeKa* and *ZnKa*, compared to those of the reference substances: synthetic  $\text{Ag}_2\text{S}$ , ( $\text{Ag}_{0.9}\text{Au}_{0.1}$ ),  $\text{Ag}(\text{Cl}_{0.8}\text{Br}_{0.1}\text{I}_{0.1})$ ,  $\text{Ag}_2\text{Te}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CdS}$ ,  $\text{Co}$ ,  $\text{GeSe}$ ,  $\text{HgS}$ ,  $\text{Ni}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnO}$ ,  $\text{ZnS}$  and natural  $\text{PbS}$ ,  $\text{CuFeS}_2$  and  $\text{FeAsS}$ . The element contents were calculated by the ZAF and Multi (Trincavelli and Castellano 1999) programs. The XRD determinations were made by the X'Pert PRO MPD device with *CuKa* radiation. The investigated mineral was separated from the polished sample thin slice by microscope hardness tester with diamond indenter in reflected light and next powdered by microscope crushing stage (Roedder 1984, pp. 212–219). The powder was glued on the glass fibre surface and then used as the XRD preparation. Some polished preparations were etched by aqueous solution of citric acid and  $\text{KNO}_3$ . Fluid inclusions in associating minerals were studied by the heating-freezing conventional method (Crawford 1981; Kozłowski 1984; Roedder 1984) and if the inclusion size was very small – by the immersion method with use of the fluids: silicone oil (boiling temp. 315°C) for heating and ethanol (melting temp. -114.1°C) for freezing (Karwowski *et al.* 1979). Accuracy of estimation for Th was  $\pm 0.5^\circ\text{C}$  and for Tm  $\pm 0.1^\circ\text{C}$ . Some inclusions were opened by indentation or in crushing stage and chemical composition of the precipitate of inclusion fluid was determined by EPMA. It was not possible to make good quality photographs of eu- and subhedral crystals of the investigated 'microminerals', thus very exact drawings were prepared by AK on the basis of binocular observations (see captions to figures further in the text). The investigations were made in the laboratories of University of Warsaw, Poland, and the University of Tübingen, Germany.

## RESULTS

Field work for 32 years in the eastern part of the Karkonosze pluton has resulted in the collection of samples containing 20 minerals – compounds of silver, mostly found in this region for the first time. Studies of the samples revealed 5 sulphides (acanthite, argentite, balkanite, canfieldite, stromeyerite), 1 arsenide (novákite), 6 sulphosalts (argyrodite, frei-

Mineral/occurrence		d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
Acanthite	Michałowice	3.05	30	2.83	65	2.60	100	2.43	65	2.44	30	2.19	35	2.09	35
	Miedziane Skały Mt.	3.06	35	2.83	50	2.58	100	2.46	60	2.39	35	2.17	30	2.08	40
	Rybień Mt.	3.06	40	2.81	55	2.60	100	2.44	60	2.43	40	2.20	30	2.08	40
	Splawna Hill	3.07	35	2.85	60	2.63	100	2.42	70	2.40	35	2.18	30	2.11	35
	Szklarska Poręba Huta	3.04	30	2.82	60	2.61	100	2.45	65	2.42	40	2.21	25	2.07	30
Guanajuato (1)	3.06	30	2.84	50	2.59	100	2.45	70	2.39	40	2.21	30	2.09	40	
Aguilarite	Miedziane Skały Mt.	3.10	50	2.86	60	2.63	90	2.60	65	2.45	100	2.39	80	2.23	45
	San Carlos mine (2)	3.09	52	2.87	58	2.62	95	2.60	63	2.45	100	2.42	86	2.22	43
Argyrodite	Splawna Hill	3.13	25	3.03	100	2.64	40	2.42	35	2.05	30	1.861	55	1.760	20
	Machacamarcia (3)	3.14	30	3.02	100	2.66	40	2.44	30	2.03	30	1.863	50	1.764	20
Balkanite	Krowia Kopa Mt.	3.07	65	2.98	95	2.62	70	2.57	100	2.44	80	1.986	70	1.953	90
	Sedmochislenitsi (4)	3.09	70	2.98	100	2.61	80	2.55	100	2.45	80	1.985	80	1.955	90
Canfieldite	Splawna Hill	3.30	16	3.16	100	2.52	10	2.24	13	2.12	20	1.935	21	1.862	20
	Lengenbach (5)	3.317	15	3.176	100	2.524	12	2.245	11	2.117	19	1.945	24	1.860	20
Cervelleite	Popiel Mt.	6.28	70	4.98	100	4.68	50	4.23	90	3.759	50	2.753	20	2.599	30
	Bambolla mine (6)	6.29	70	5.00	100	4.64	40	4.24	90	3.766	50	2.753	10	2.596	30
Chlorargyrite	Cicha Równia Mt.	3.20	30	2.77	100	1.94	50	1.65	20	1.25	45	1.14	30	0.94	20
	synthetic (7)	3.216	25	2.764	100	1.957	55	1.668	15	1.244	50	1.138	30	0.921	20
Freieslebenite	Wolek Mt.	3.40	70	3.24	30	2.96	85	2.81	100	2.05	45	1.99	30	1.77	60
	Příbram (8)	3.486	75	3.244	25	2.972	80	2.824	100	2.069	40	1.994	35	1.789	55
Matildite	Ptak Hill	3.29	75	3.11	25	2.84	100	2.04	60	1.95	60	1.70	35	1.25	30
	Camsell River (9)	3.302	80	3.116	20	2.827	100	2.029	50	1.966	60	1.709	30	1.246	30
Muthmannite	Kowska Czuba Mt.	4.43	100	3.35	85	2.57	30	2.50	40	2.21	40	1.854	20	1.423	20
	calculated (10)	4.419	100	3.346	93	2.562	24	2.488	38	2.210	43	1.859	24	1.423	18
Naumannite	Miedziane Skały Mt.	2.87	15	2.64	100	2.56	100	2.40	30	2.25	55	2.09	30	1.98	35
	Tilkerode (11)	2.88	10	2.66	100	2.56	100	2.42	20	2.23	60	2.07	20	2.00	40
Novákite	Granicznik Mt.	1.995	75	1.953	85	1.878	100	1.348	60	1.223	65	1.176	85	1.155	45
	Obří Důl (12)	1.998	80	1.959	90	1.877	100	1.351	60	1.225	60	1.180	90	1.157	50
Owyheelite	Michałowice	3.49	65	3.36	35	3.24	100	2.89	45	2.82	50	2.33	35	2.08	40
	Poorman mine (13)	3.49	70	3.37	40	3.25	100	2.90	50	2.84	60	2.23	50	2.05	60
Proustite	Kowska Czuba Mt.	3.25	85	3.20	100	3.09	40	2.745	75	2.553	70	2.492	65	1.927	35
	synthetic (14)	3.28	90	3.19	100	3.12	40	2.744	80	2.557	70	2.490	70	1.925	30
Pyrrargyrite	Krowia Kopa Mt.	3.34	75	3.24	90	3.21	65	2.782	100	2.562	95	2.535	85	1.960	45
	synthetic (14)	3.34	80	3.22	90	3.18	70	2.779	100	2.566	97	2.532	90	1.957	50
Stromeyerite	Miedziane Skały Mt.	3.29	55	2.61	100	2.04	55	1.989	35	1.883	50	1.737	40	1.421	30
	Piaskowa Mt.	3.27	60	2.62	100	2.05	60	1.991	40	1.885	45	1.735	40	1.417	35
	Gowganda (15)	3.28	55	2.61	100	2.03	55	1.988	45	1.881	50	1.738	45	1.420	35
Stützite	Popiel Mt.	3.54	65	3.51	60	3.01	75	2.63	70	2.53	85	2.15	100	2.09	55
	May Day mine (16)	3.55	60	3.52	60	3.02	75	2.63	65	2.54	80	2.17	100	2.10	55
Tsnigriite	Piaskowa Mt.	4.26	45	3.79	75	2.90	45	2.85	45	2.28	40	2.21	100	2.08	35
	Bełtau Mts. (17)	4.26	50	3.78	70	2.89	40	2.85	40	2.29	40	2.20	100	2.10	40
Volynskite	Szklarska Poręba Huta	3.11	100	2.22	45	2.16	35	1.99	15	1.83	25	1.73	10	1.54	15
	Sotk (Zod) deposit (18)	3.09	100	2.21	50	2.15	30	1.98	10	1.82	30	1.73	10	1.55	20

Table 1. X-ray powder diffraction patterns of the silver minerals from the Karkonosze pluton. The selection of the most intense reflections of the samples is shown; intensity values are recalculated to the 100-grade scale when necessary. Numbers in the parentheses pertain to the following references: (1) Petruk *et al.* (1974), (2) Bindi and Pingitore (2013), (3) Ahlfeld and Moritz (1933), (4) Atanassov and Kirov (1973), (5) Bindi *et al.* (2012), (6) Criddle *et al.* (1989), (7) authors' data from 2009, (8) authors' data from 2011, (9) Harris and Thorpe (1969), (10) Bindi and Cipriani (2004), (11) Earley (1950), (12) Johan and Hak (1961), (13) Robinson (1949), (14) Toulmin (1963), (15) Frueh Jr. (1954), (16) authors' data from 2016, (17) Sandomirskaya *et al.* (1992), and (18) Bayliss (1991).

eslebenite, matildite, owyheelite, proustite, pyrrargyrite, 7 selenides and tellurides (aguilarite, naumannite, cervelleite, muthmannite, stützite, tsnigriite, volynskite) and 1 chloride (chlorargyrite). The specimens are very small – from tenths of a millimetre

to a few millimetres ('microminerals'). They were identified by X-ray diffraction (Table 1) and EPMA (Tables 2–4) methods, and the data in the tables are representative. Acid etching of the minerals was used as a supporting method.

### Acanthite $\alpha$ -Ag<sub>2</sub>S<sup>1</sup>

The mineral of silver sulphide composition was known in the past as *Glaserz* (*Glaßerz*), *Silberglaserz* or *Silberglanz* (see e.g., Agricola 1558 or Jonas 1820). The monoclinic variety of silver sulphide (point group 2/m) was identified in ore from Jáchymov and named acanthite by Kennigott (1855a, b). The monoclinic structure of Ag<sub>2</sub>S is stable below +177°C, thus if it formed as acanthite, the crystallization occurred at low-temperature.

In this study a euhedral specimen of acanthite was found at Rybień Mt.; it forms a parallel growth of two elongated crystals (Text-fig. 2). Such a habit is typical of acanthite (this is why the name is derived from Greek *ἀκανθα*, i.e., thorn). On the basis of the chemical analysis (no. 07 in Table 2) the calculated formula was as follows: (Ag<sub>1.88</sub>Cu<sub>0.04</sub>Pb<sub>0.03</sub>Sb<sub>0.01</sub>)<sub>Σ1.96</sub>(S<sub>0.99</sub>Se<sub>0.01</sub>)<sub>Σ1.00</sub>. Primary acanthite, i.e., precipitated as  $\alpha$ -Ag<sub>2</sub>S, was also found in the outcrops at Michałowice (Text-fig. 3A), Piaskowa Mt. (Text-fig. 3B) and Szklarska Poręba Huta (Text-fig. 3C). The first forms anhedral grains of composition (Ag<sub>1.95</sub>Cu<sub>0.02</sub>Fe<sub>0.01</sub>Pb<sub>0.01</sub>)<sub>Σ1.99</sub>(S<sub>0.99</sub>Se<sub>0.01</sub>)<sub>Σ1.00</sub> (analysis no. 02 in Table 2), the second – acicular ‘thorn’ crystals with formula (Ag<sub>1.95</sub>Cu<sub>0.02</sub>Fe<sub>0.01</sub>Pb<sub>0.01</sub>)<sub>Σ1.99</sub>(S<sub>0.99</sub>Se<sub>0.01</sub>)<sub>Σ1.00</sub> (analysis No. 06 in Table 2) and the third – anhedral grains that have the composition (Ag<sub>1.91</sub>Cu<sub>0.05</sub>Pb<sub>0.02</sub>Zn<sub>0.01</sub>Cd<sub>0.01</sub>)<sub>Σ1.97</sub>(S<sub>0.99</sub>Se<sub>0.01</sub>)<sub>Σ1.00</sub> (analysis no. 10 in Table 2). The central parts of these three specimens are formed by post-argentite paramorphs and are described below. Small grains of acanthite of composition (Ag<sub>1.93</sub>Cu<sub>0.03</sub>Fe<sub>0.02</sub>Sn<sub>0.02</sub>)<sub>Σ2.00</sub>(S<sub>0.99</sub>Se<sub>0.01</sub>)<sub>Σ1.00</sub> were found at Sławna Hill with cassiterite, pyrite, chalcopyrite and canfieldite (see text-figure in the paragraph on canfieldite; analysis no. 08 in Table 2). Miedziane Skały Mt. was the source of the next specimen, with acanthite occurring in association with pyrite, galena, tetrahedrite, aguilarite and naumannite. This acanthite has two different compositions in neighbouring grains (see text-figure in the paragraph on aguilarite) – without replacement of sulphur by selenium (Ag<sub>1.89</sub>Cu<sub>0.03</sub>Fe<sub>0.03</sub>Pb<sub>0.04</sub>)<sub>Σ1.99</sub>S<sub>1.00</sub> (analysis no. 04 in Table 2), and with this replacement, as seen in the formula (Ag<sub>1.82</sub>Cu<sub>0.09</sub>Fe<sub>0.04</sub>Zn<sub>0.03</sub>)<sub>Σ1.98</sub>(S<sub>0.97</sub>Se<sub>0.03</sub>)<sub>Σ1.00</sub> (analysis no. 03 in Table 2). Probably it is a result of a change of the parent solution of the minerals, which



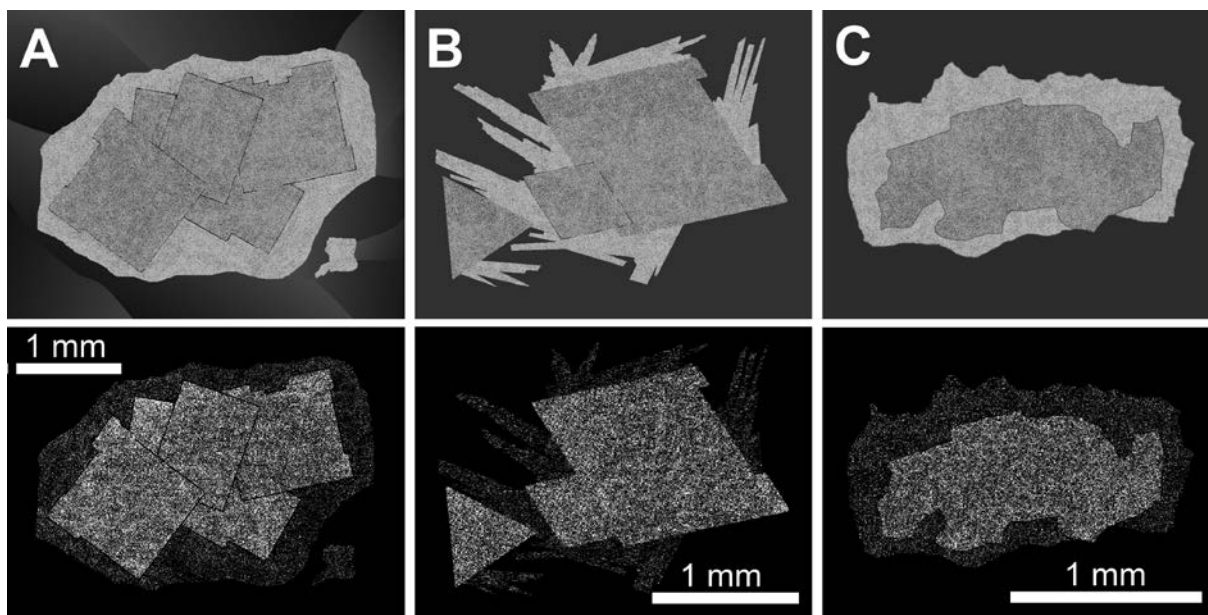
Text-fig. 2. Acanthite, drawing of two euhedral parallel crystals; Rybień Mt.

depended on inflow of fluid with some Se or a shift of the physical parameters that allowed or suspended the Se included in the acanthite structure. Acanthite was also found in another specimen from Piaskowa Mt. in association with pyrite, galena, stromeyerite and tsnigriite, but it was not analysed quantitatively.

### Argentite $\beta$ -Ag<sub>2</sub>S

The stability of the isometric  $\beta$ -Ag<sub>2</sub>S phase above +177°C (Ramsdell 1925; Emmons *et al.* 1926) and rapid transition below this temperature to the monoclinic  $\alpha$ -Ag<sub>2</sub>S structure (Sadanaga and Sueno 1967; Sadovnikov and Gerasimov 2019) cause that the investigated Ag<sub>2</sub>S specimens are presently acanthite. Those which had crystallized as argentite became post-argentite acanthite paramorphs (Text-figs 3 and 4). Only habits of euhedral crystals typical of the isometric system may suggest that the Ag<sub>2</sub>S mineral was originally argentite. From among the collected specimens three had this feature. The most perfect isometric habit was a feature of a specimen from Szklarska Poręba Huta (Text-fig. 4) that consisted of four octahedrons one on another connected according to the (100) plane from largest to the smallest. Faces of the smallest octahedron are of the window type; this attribute and the decreasing size of the octahedrons indicate that the content of silver in the parent fluid of the minerals decreased. The mineral composition

<sup>1</sup> Formulae of the minerals given in the section titles are ideal; chemical analyses of the investigated mineral specimens were converted to the individual formulae (see text) with use of the proper numbers of anions.



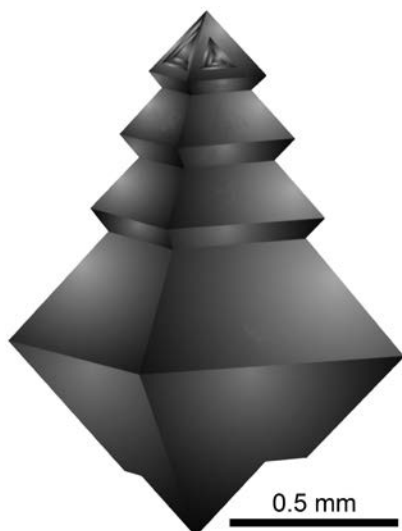
Text-fig. 3. Primary acanthite surrounding the acanthite post-argentite paramorph; photos of the polished preparations etched by aqueous solution of citric acid and  $\text{KNO}_3$  taken in the reflected-oblique light (upper series) and the  $\text{CuK}\alpha$  images of the same fields; A – Michałowice, B – Piaskowa Mt., C – Szklarska Poręba Huta.

Mineral / occurrence	No.	Ag	Cu	Fe	Zn	Cd	Hg	Sn	Pb	As	Sb	S	Se	Te	$\Sigma$
Acanthite															
Michałowice	01	76.14	3.43	1.62					3.44		1.01	12.78	0.98	0.53	99.93
	02	85.21	0.51	0.23					0.84			12.86	0.32		99.97
Miedziane Skały Mt.	03	81.86	2.38	0.93	0.82				tr.			12.98	0.99		99.96
	04	82.24	0.77	0.68					3.34			12.94			99.97
Piaskowa Mt.	05	81.96	1.21	0.52	0.48			0.38	0.67		0.44	12.55	0.54	1.23	99.98
	06	84.98	0.57	0.30					0.92			12.79	0.39		99.95
Rybień Mt.	07	82.62	1.04						2.53		0.50	12.94	0.32		99.95
Splawna Hill	08	84.57	0.78	0.46				0.96				12.90	0.31		99.98
Szklarska Poręba Huta	09	79.49	2.86		0.27	0.46			3.38			12.87	0.66		99.99
	10	80.78	1.82		1.07	1.38	0.82					12.59	0.97	0.51	99.94
	11	79.42	1.54	0.90	0.79		0.81	0.48	1.68		0.99	12.72	0.64	tr.	99.97
Balkanite															
Krowia Kopa Mt.	12	33.74	36.23	0.25			11.88		1.32	0.33		16.20			99.95
Canfieldite															
Splawna Hill	13	72.41	0.37					9.50	0.53	0.32	0.62	16.23			99.98
Novákite															
Granicznik Mt.	18	4.67	59.06	0.03	0.04*	0.02**			0.07	36.05		0.05			99.99
Stromeyerite															
Granicznik Mt.	14	48.93	32.95	0.64	0.36				0.92			15.83	0.36		99.99
Miedziane Skały Mt.	15	45.79	30.40	0.83			4.98	1.07	0.90			14.84	0.64	0.52	99.97
Piaskowa Mt.	16	49.42	29.43	0.62	0.41		2.11	1.03	0.83			15.00	0.61	0.48	99.94
	17	47.87	28.56	0.31				0.51	4.16		2.16	14.39	0.41	1.60	99.97

Table 2. Chemical composition of the silver sulphides and arsenides, in wt. %; empty cells – component below detection limit ( $< \sim 0.001$  wt%); analyses nos. 01, 05, 09 and 11 – post-argentite paramorphs; \* Co, \*\* Ni.

is  $(\text{Ag}_{1.82}\text{Cu}_{0.06}\text{Fe}_{0.04}\text{Zn}_{0.03}\text{Pb}_{0.02}\text{Sb}_{0.02}\text{Sn}_{0.01}\text{Hg}_{0.01})_{\Sigma 2.01}$   $(\text{S}_{0.98}\text{Se}_{0.02})_{\Sigma 1.00}$  (analysis no. 11 in Table 2); it is notable that silver in the mineral (1.82 apfu) is significantly

replaced by seven other elements (0.01 to 0.06 apfu), which may have been induced by a relatively high temperature of crystallization of the primary argentite.



Text-fig. 4. Argentite (now acanthite paramorph), adherence of four euhedral crystals along the *c*-axis, the uppermost one with window-type faces, drawing; Szklarska Poręba Huta.

Three further post-argentite paramorphs were found, surrounded by primary acanthite (see above). The specimen from Michałowice (Text-fig. 3A) contained a group of cubic crystals with composition  $(\text{Ag}_{1.70}\text{Cu}_{0.13}\text{Fe}_{0.07}\text{Pb}_{0.04}\text{Sb}_{0.02})_{\Sigma 1.96}(\text{S}_{0.96}\text{Se}_{0.03}\text{Te}_{0.01})_{\Sigma 1.00}$  (analysis no. 01 in Table 2); the crystals are of various orientations and with certain window faces. The sample from Piaskowa Mt. (Text-fig. 3B) has octahedral post-argentite crystals as an inner core; one octahedron (the left one in the photograph) formed separately. Their composition, very similar within, and between, crystals is as follows:  $(\text{Ag}_{1.88}\text{Cu}_{0.05}\text{Fe}_{0.02}\text{Zn}_{0.02}\text{Pb}_{0.01}\text{Sb}_{0.01}\text{Sn}_{0.01})_{\Sigma 1.99}(\text{S}_{0.96}\text{Se}_{0.02}\text{Te}_{0.02})_{\Sigma 1.00}$  (analysis no. 05 in Table 2). But in the grain from Szklarska Poręba Huta the inner part, probably post-argentite as well, is anhedral. A significant difference occurs in chemical composition, the inner part has the formula  $(\text{Ag}_{1.81}\text{Cu}_{0.11}\text{Pb}_{0.03}\text{Zn}_{0.02}\text{Cd}_{0.01}\text{Hg}_{0.01})_{\Sigma 1.99}(\text{S}_{0.96}\text{Se}_{0.03}\text{Te}_{0.01})_{\Sigma 1.00}$  (analysis no. 09 in Table 2). Note that the paramorphs have distinctly higher contents of minor elements than the primary acanthite.

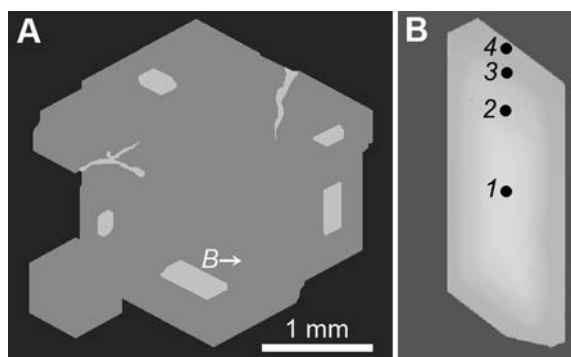
The paramorphs became visible after etching of the polished surface with aqueous solution of citric acid and potassium nitrate. The etching effect of the paramorphs was more intensive than of the primary acanthite. Two reasons for this are the supposed: presence of defects in the crystal lattice which appeared during conversion of the crystal structure from isometric to monoclinic, and the presence of lower concentrations of trace elements in primary

acanthite than in the former argentite, as is shown in the lower series of photos in Text-fig. 3, which display the images of distribution of  $\text{CuK}\alpha$  excited by the electron beam. Not only is the abundance of Cu higher in the paramorphs, but also the amounts of Fe, Zn, Cd, Pb and Se; moreover, Sb, Hg and Te occur additionally (analyses nos. 01, 05 and 09 in Table 2). The specimen from Szklarska Poręba Huta (Text-fig. 3C) does not have a euhedral inner core, but the more intensive etching of this part of the grain than its outer rim may support the suggestion that it is a post-argentite paramorph.

### Balkanite $(\text{Cu}_{9-x}\text{Me}_{2+x})\text{Ag}_{5-x}\text{HgS}_8$

The first specimen of balkanite was found in 1961 in Bulgaria, at Stara Planina in the Balkan Mts, in the Sedmochislenitsi mine within a Pb-Zn-Cu stratiform deposit (Atanassov and Kirov 1973). The proposed chemical formula was  $\text{Cu}_9\text{Ag}_5\text{HgS}_8$ , next modified by Biagnoni and Bindi (2017) to  $(\text{Cu}_{9-x}\text{Me}_{2+x})\text{Ag}_{5-x}\text{HgS}_8$ . The balkanite structure belongs to the space group P2/m of the monoclinic system. It was found in a number of ore occurrences; the Schwarzleo polymetallic deposit in Salzburg province, Austria, is a good example. Balkanite occurs there mostly as anhedral intergrowths with other ore minerals, but euhedral prismatic crystals were also noted (Paar and Chen 1985).

Balkanite from Krowia Kopa Mt. occurs as euhedral prismatic inclusions in chalcopyrite, arranged in a growth zone (Text-fig. 5A). Moreover, it formed tiny 'veinlets' in the host mineral roughly in accordance with the growth direction of chalcopyrite. This suggests a certain period of stability of the conditions (chemical and physical) favourable for balkanite crystallization.



Text-fig. 5. Balkanite inclusions in chalcopyrite (A) and one of the crystals of balkanite with zoning visible due to appropriate contrast of the image (B), 1–4 – EPMA points, BSE images; Krowia Kopa Mt.



The studied balkanite crystals have a quite constant chemical composition (analysis no. 12 in Table 2). The formula  $(\text{Ag}_{4.91}\text{Cu}_{8.95}\text{Pb}_{0.10}\text{Fe}_{0.07}\text{Hg}_{0.93})_{\Sigma 14.96}(\text{S}_{7.93}\text{As}_{0.07})_{\Sigma 8.00}$  shows minor differences with regard to that one proposed by Atanassov and Kirov (1973). The crystals have a very subtle zoning of composition with a little higher silver content in the central part than in the outer zone (Text-fig. 5B). The determined Ag amounts are (in wt. %): point 1 – 33.89, point 2 – 33.71, point 3 – 33.54, and point 4 – 33.41. This may indicate a slow decrease of the silver available for crystallization of the mineral, and the scheme of zoning suggests crystallization of balkanite crystals without contact with the chalcopyrite grain. Probably the already euhedral balkanite crystals stuck to chalcopyrite and next they were trapped in it.

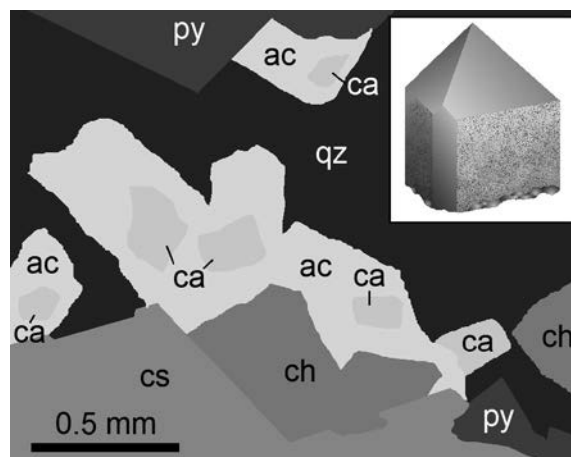
### Canfieldite $\text{Ag}_8(\text{Sn,Ge})(\text{S,Te})_6$

This mineral (orthorhombic, class mm2) was first recognized in ore specimens brought from Colquechaca in Chayanta province, Bolivia, to S.L. Penfield, who investigated it and published the results (Penfield 1893), though probably with an error in the analysis of the mineral. Problems in recognizing this new mineral were raised by Prior and Spencer (1898). The replacement of Sn by Ge (e.g., Lunt 1923) and of S by Te (cf. Harris and Owens 1971; Bindi *et al.* 2012) or Se (Zhai *et al.* 2019) were studied many times afterwards.

Canfieldite from Sławna Hill occurs in association with cassiterite, chalcopyrite, pyrite and acanthite, the latter mostly as anhedral inclusions 0.2–0.3 mm in size. However, a subhedral crystal c. 1 mm high with clear orthorhombic symmetry and faces  $\{100\}$ ,  $\{hk0\}$  and  $\{hkl\}$  was found in the same sample (Text-fig. 6). The chemical composition of the canfieldite crystals in the investigated sample practically does not vary and analysis no. 13 (Table 2) is representative. Neither Ge nor Te or Se was found. The calculated chemical formula  $(\text{Ag}_{7.89}\text{Cu}_{0.07}\text{Pb}_{0.03}\text{Sn}_{0.94}\text{Sb}_{0.06})_{\Sigma 8.99}(\text{S}_{5.95}\text{As}_{0.05})_{\Sigma 6.00}$  shows replacement of Ag by Cu and Pb, and of Sn by Sb; minor S is replaced by As. The chemical data suggest very stable conditions of crystallization of the canfieldite-bearing mineral association.

### Stromeyerite $\text{AgCuS}$

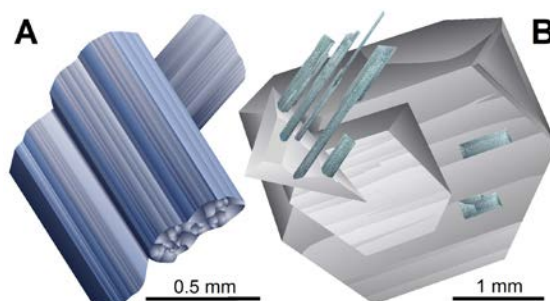
This is not a rare component of copper and silver ores, earlier called *Silberkupferglanz*. Beudant (1832, pp. 410–411) suggested the new name ‘stromeyerine’, later modified to ‘stromeyerite’. This mineral



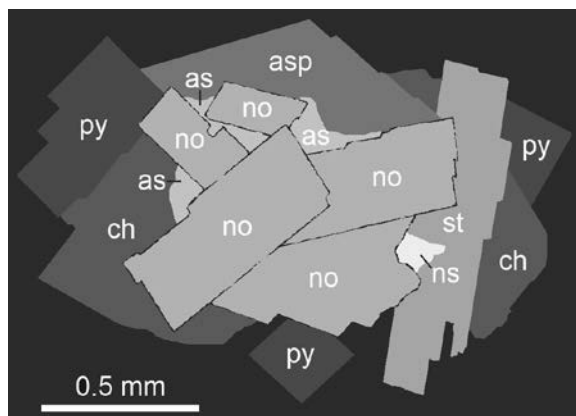
Text-fig. 6. Canfieldite (ca) associated with cassiterite (cs), acanthite (ac), chalcopyrite (ch) and pyrite (py) in quartz (qz), BSE image; insert – drawing of subhedral canfieldite crystal 1 mm high; Sławna Hill.

is orthorhombic (class mmm); its structure was investigated by Frueh Jr. (1954) and Djurle (1958). The stromeyerite habit is commonly euhedral, even in growth with other minerals. Its faces usually have a bluish coating of various tints.

In the specimens collected for this research, stromeyerite was found in four samples: from Miedziane Skały Mt. and Piaskowa Mt. (both in Text-fig. 7), the third specimen also from Piaskowa Mt. (see text-figure in the paragraph on tsnigriite) and the fourth from Granicznik Mt. (Text-fig. 8). Stromeyerite from Miedziane Skały Mt. crystallized on euhedral crystals of a tetrahedrite group mineral as rods on the base crystal faces either oblique to them or grown flat on another face. One specimen from Piaskowa Mt. was formed by two parallel growths of the prismatic crystals joined obliquely. Another sample from Piaskowa Mt. contains stromeyerite of a nearly dendritic habit, associated with acanthite, galena, pyrite



Text-fig. 7. Stromeyerite drawings. A – group of crystals, Piaskowa Mt. (Kozłowski *et al.* 2016) and B – crystals (bluish) on tetrahedrite-group mineral, Miedziane Skały Mt. in Hutniczy Ridge.



Text-fig. 8. Novákite (no) in the mineral assemblage with native arsenic (as), native silver (ns), pyrite (py), chalcopyrite (ch), arsenopyrite (asp) and stromeyerite (st), background – quartz; BSE image; Granicznik Mt.

and tsnigriite. A similar habit has stromeyerite from Granicznik Mt., and novákite, native silver, native arsenic, pyrite, chalcopyrite and arsenopyrite are the co-occurring minerals. Chemical formulae calculated on the basis of EPMA data (Table 2) are as follows (in sequence of the above described samples):

- Granicznik Mt. ( $\text{Ag}_{0.91}\text{Cu}_{1.04}\text{Fe}_{0.02}\text{Pb}_{0.01}\text{Zn}_{0.01}$ ) $\Sigma$ 1.99 ( $\text{S}_{0.99}\text{Se}_{0.01}$ ) $\Sigma$ 1.00 (analysis no. 14);
- Miedziane Skały Mt. ( $\text{Ag}_{0.89}\text{Hg}_{0.05}\text{Fe}_{0.03}\text{Sn}_{0.02}\text{Pb}_{0.01}$ ) $\Sigma$ 1.00 ( $\text{Cu}_{0.97}\text{Se}_{0.02}\text{Te}_{0.01}$ ) $\Sigma$ 1.00 (analysis no. 15);
- Piaskowa Mt. ( $\text{Ag}_{0.95}\text{Cu}_{0.96}\text{Hg}_{0.02}\text{Fe}_{0.02}\text{Sn}_{0.02}\text{Zn}_{0.01}\text{Pb}_{0.01}$ ) $\Sigma$ 1.99 ( $\text{S}_{0.97}\text{Se}_{0.02}\text{Te}_{0.01}$ ) $\Sigma$ 1.00 (analysis no. 16);
- Piaskowa Mt. ( $\text{Ag}_{0.95}\text{Cu}_{0.95}\text{Pb}_{0.04}\text{Sb}_{0.04}\text{Fe}_{0.01}\text{Sn}_{0.01}$ ) $\Sigma$ 2.00 ( $\text{S}_{0.96}\text{Te}_{0.03}\text{Se}_{0.01}$ ) $\Sigma$ 1.00 (analysis no. 17).

The main cations are replaced by a common element (Fe), however rarer ones like Hg, Sn, etc. appear as minor components. Three samples have a substitution of 0.03–0.04 apfu of S by selenide and telluride anions; Te is absent only in stromeyerite from Granicznik Mt.

### Novákite $\text{Cu}_{20}\text{AgAs}_{10}$

The mineral was first found at Černý Důl mine in the Trutnov district near Hradec Králové, Czechia, at the end of the 1950s (Johan and Hak 1959, 1961; Johan 1985). The occurrence of such a mineral at this locality was confirmed by Doubek (1999). Cashin mine in the La Sal mining district, Colorado, USA, was another place where this mineral was recorded (Eckel 1997). Novákite is monoclinic (space group not determined exactly), but the habits of its crystals were not presented in the above publications.

The specimen from Granicznik Mt. contains five approximately euhedral crystals of this mineral, surrounded by grains of native silver, native arsenic, chalcopyrite, stromeyerite, arsenopyrite and pyrite (Text-fig. 8). Native arsenic was noted as an associate replaced by novákite (Johan and Hak 1961), but in the sample presented here this phenomenon is not obvious. Nevertheless, the co-occurrence of two As minerals, especially native arsenic with this arsenide points to a crystallization environment rich in As, though in these novákite crystals minor replacement of As by S was found. However, the chemical composition of the novákite is typical, with minor admixtures of Fe, Co, Ni and Pb (analysis no. 18 in Table 2). The chemical data were recalculated to the formula  $(\text{Cu}_{20.02}\text{Ag}_{0.93}\text{Fe}_{0.01}\text{Co}_{0.01}\text{Ni}_{0.01}\text{Pb}_{0.01})\Sigma 20.99(\text{As}_{9.97}\text{S}_{0.03})\Sigma 10.00$ .

### Argyrodite $\text{Ag}_8\text{Ge}(\text{S},\text{Se})_6$

Argyrodite was recognized as a new mineral in an ore specimen from Himmelsfürst mine at Brand-Erbisdorf near Freiberg, Germany; the new element germanium was found also during its analysis (Weisbach 1886a, b). The problem of the presence of Sn (possibly replacing Ge) in argyrodite from Bolivia was discussed by Penfield (1894), Prior and Spencer (1898), and Ahlfeld and Moritz (1933). Recently, information was published on argyrodite from Roşia Montană, Romania, which had a high content of selenium (Tămaş *et al.* 2006).

Argyrodite crystals are orthorhombic (class mm2). The euhedral specimen from Splawna Hill presents this symmetry very well and has a typical dark grey colour (Text-fig. 9). The euhedral habit is slightly disturbed by slats of the same mineral par-



Text-fig. 9. Argyrodite, drawing of euhedral crystal with parallel crystallized slats of the same mineral; Splawna Hill.

Mineral / occurrence	No.	Ag	Cu	Pb	As	Sb	Bi	Fe	Ge	S	Se	Te	Σ
Argyrodite													
Splawna Hill	19	75.71	0.16	0.33*				0.15**	6.29	16.86	0.27	0.21	99.98
Freieslebenite													
Wolek Mt.	20	19.63	0.32	38.32		22.35	0.82	0.11		17.83	0.27	0.31	99.96
Matildite													
Ptak Hill	21	27.57	0.42		0.81	0.29	54.32			16.56			99.97
Owyheelite													
Michałowice	22	7.37	0.24	42.75	0.51	28.84	1.03			19.24			99.98
Proustite													
Kowarska Czuba Mt.	23	64.04	0.54	0.46	14.66	0.53				19.22	0.49	tr.	99.94
Pyrargyrite													
Krowia Kopa Mt.	24	59.03	0.24	0.46	0.16	22.19				17.63	0.12	0.14	99.97

Table 3. Chemical composition of the silver sulphosalts, in wt. %; empty cells – component below detection limit (< ~0.001 wt%); \* Hg, \*\* Sn.

allel to the *C* axis on the prism faces. The chemical composition (analysis no. 19 in Table 3) includes small amounts of Hg (0.33 wt. %). Contents of Sn (0.15 wt.%), Se (0.27 wt. %) and Te (0.21 wt. %) are low. The calculated formula ( $\text{Ag}_{7.93}\text{Cu}_{0.03}\text{Hg}_{0.02}$ ) $\Sigma_{7.98}(\text{Ge}_{0.98}\text{Sn}_{0.01})\Sigma_{0.99}(\text{S}_{5.94}\text{Se}_{0.04}\text{Te}_{0.02})\Sigma_{6.00}$  has no unusual features.

### Freieslebenite $\text{AgPbSbS}_3$

The first description of a mineral from the Freiberg region, named *Schilfglaserz*, was published by Johann Carl Freiesleben in the catalogue of his collection (Freiesleben 1817). The name freieslebenite was given much later (Haidinger 1845, p. 569). Afterwards, Reuss's description (1860, with chemical analyses made by von Payr) of this mineral newly found in the polymetal deposit at Příbram (Czechia) became available, compared with the data from Freiberg (Germany) and Hiendelaencina (Spain;

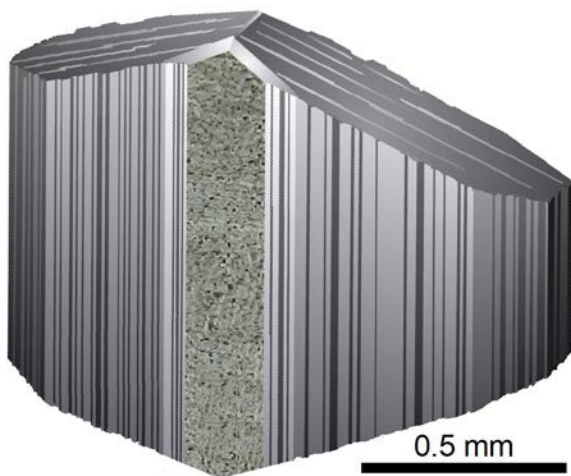
cf. Martinez Frias 1992); for these deposits analyses were made by Wöhler and Escosura (first names not given). Moreover, Zepharovich (1871) published a review of the data on freieslebenite available at that time. The structure of this mineral was explored by Hellner (1957), Ito and Nowacki (1974), and Berlepsch *et al.* (2002).

Freieslebenite crystallizes in the monoclinic system, prismatic class 2/m. The specimen from Wolek Mt. has the typical habit (Text-fig. 10) of a combination of monoclinic prisms and pinacoids. The faces {010} are rough, and the other ones are ribbed. This striation was in part caused by twinning lamellae. Analysis no. 20 is typical, with minor amounts of Cu and Fe replacing Ag and Pb, and with some Bi in the Sb sites. In small part S is also substituted by Se and Te. The chemical formula is: ( $\text{Ag}_{0.97}\text{Pb}_{0.99}\text{Cu}_{0.03}\text{Fe}_{0.01}$ ) $\Sigma_{2.00}(\text{Sb}_{0.98}\text{Bi}_{0.02})\Sigma_{1.00}(\text{S}_{2.97}\text{Se}_{0.02}\text{Te}_{0.01})\Sigma_{3.00}$ .

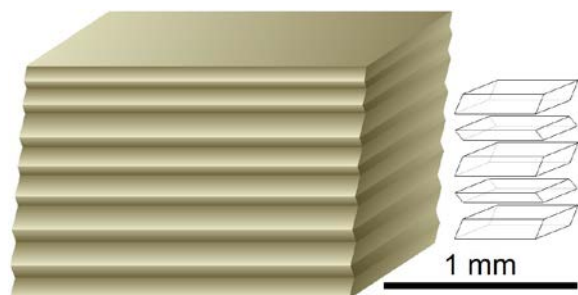
### Matildite $\beta\text{-AgBiS}_2$

Matildite was described for the first time by Rammelsberg (1877) in a specimen collected in the Matilda mine (near Morococha in Yauli province of the Junin region, Peru) and that time the name used for this mineral was *Silberwismuthglanz*. It crystallizes in the trigonal system, trapezohedral class 32. Data on its structure and observed intergrowths with e.g., galena, were published by Graham (1951), and Harris and Thorpe (1969), later extended by Bayliss (1991).

The specimen of matildite from Ptak Hill crystallized as a parallel growth of rhombohedral plates of almost the same sizes; the face of a rhombohedron is the plane of plates contact (Text-fig. 11; note the scheme of the plate positions in this figure). The surface of the matildite specimen has a very thin coating of bismite, which results in a yellowish tint



Text-fig. 10. Freieslebenite, drawing of a crystal with ribbed faces; Wolek Mt.



Text-fig. 11. Matildite, drawing of multiple-twin grain with very thin coating of bismite and a scheme of the flat rhombohedral crystals forming the twinning; Ptak Hill.

but still does not hide the metallic lustre of the sulphosalt. Admixtures in the chemical composition of this matildite specimen are moderate (analysis no. 21 in Table 3) – 0.42 wt. % Cu for Ag, 0.29 wt. % Sb for Bi and 0.81 wt. % As for S, thus  $(\text{Ag}_{0.97}\text{Cu}_{0.02})_{\Sigma 0.99}(\text{Bi}_{0.99}\text{Sb}_{0.01})_{\Sigma 1.00}(\text{S}_{1.96}\text{As}_{0.04})_{\Sigma 2.00}$  is the calculated formula. Matildite was also found in the Karkonosze pluton in the Szklarska Poręba Huta (Łukasz Karwowski, pers. comm., 2021).

### Owyheeite $\text{Ag}_{3+x}\text{Pb}_{10-2x}\text{Sb}_{11+x}\text{S}_{28}$

The earliest mention of this mineral was most probably published by Burton (1868); he found it in ore from the Sheba mine near Star City in Nevada. Its name in that publication is argentiferous jamesonite. Later it was discovered again (Shannon 1921,

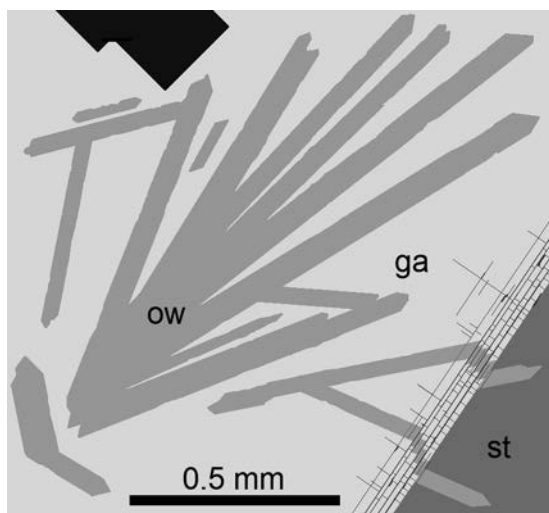
1926) and described as owyheeite. The name was proposed from Owyhee County in Idaho, in which the Poorman Mine near Silver City is located, where the mineral was found. Robinson (1949) suggested that the publications of both authors refer to specimen(s) from the same location in museum collections. He also published his own data on the structure of owyheeite. This mineral is commonly defined as occurring only rarely (e.g., by Asher 1968).

Owyheeite is monoclinic (prismatic class 2/m) with habits of hairs, wires or thin rods. In the specimen from Michałowice, owyheeite forms radial groups of crystals of lath habit overgrown with galena and stibnite (Text-fig. 12). Probably owyheeite crystallized earlier than galena and stibnite, because the direction of its crystals does not show an influence of the structure of the surrounding minerals. Moreover, its two crystals penetrate both galena and stibnite. Stibnite adjacent to galena had shifted after crystallization, thus causing cleavage cracks in galena and stepped deformation of the owyheeite crystals. This is a record of late disturbance of a calm environment of mineral crystallization.

The chemical composition of the owyheeite crystals (analysis no. 22 in Table 3) shows neither zoning in them nor differences between them. The additional amount of Ag is 0.15 apfu, and 0.17 Cu apfu replaces Pb, moreover 0.23 Bi apfu is in the sites of Sb. In the S sites 0.31 As apfu was found, thus the formula is  $\text{Ag}_{3.15}(\text{Pb}_{9.52}\text{Cu}_{0.17})_{\Sigma 9.69}(\text{Sb}_{10.93}\text{Bi}_{0.23})_{\Sigma 11.16}(\text{S}_{27.69}\text{As}_{0.31})_{\Sigma 28.00}$ .

### Proustite $\text{Ag}_3\text{AsS}_3$

Proustite was a component of the silver ores exploited even a long time ago, when its name was *argentum rude rubrum* (Agricola 1558, p. 362), *Rothgülden* Ertz (Valentinus 1676, p. 52), *Rothgülden* (Henckel 1725, p. 185) or *rothgiltig Erz* (Lasius 1789, pp. 104, 308, 323). Beudant (1832, p. 430) added the names *Rubinblende*, *argent rouge*, *argent antimonié sulfuré* that could be used for the arsenic and antimony sulphosalts of silver and finally proposed proustite for the arsenic sulphosalt. Pink-red proustite-pyrargyrite mineralization was for centuries a good indicator in prospecting for silver ore deposits. An exhaustive review of the published data on proustite (and pyrargyrite) until the issue year was prepared by Rethwisch (1886). Studies of the chemical composition and morphological features of the proustite crystals were performed by Miers and Prior (1887) and Miers (1888). Bindi *et al.* (2010) discussed the structure of crystals of the proustite–pyrargyrite series.



Text-fig. 12. Owyheeite (ow) that formed a bundle of crystals in galena (ga) and stibnite (st), black – gangue mineral, note the cleavage cracks and grain shift along the galena-stibnite contact, BSE image; Michałowice.

Proustite is trigonal, ditrigonal scalenohedral  $\bar{3}2m$  class. The specimen found at Kowarska Czuba Mt. was a group of seven euhedral crystals of various sizes (0.3 to 1.4 mm). Their shape consisted of the faces of ditrigonal prism, scalenohedron and two different rhombohedrons (Text-fig. 13). Perfect habits of the crystals indicated stable physical-chemical conditions during crystallization. No differences in the chemical composition of this specimen were found (analysis no. 23 in Table 3). Silver was in a small part replaced by Cu (0.54 wt. %) and Pb (0.46 wt. %), As by Sb (0.53 wt. %), and S by Se (0.49 wt. %) plus a trace of Te. Thus it is a rather Sb-poor end-member of the proustite-pyrargyrite series with the chemical formula  $(Ag_{2.94}Cu_{0.04}Pb_{0.01})_{\Sigma 2.99}(As_{0.97}Sb_{0.02})_{\Sigma 0.99}(S_{2.97}Se_{0.03})_{\Sigma 3.00}$ .



Text-fig. 13. Proustite, drawing of a group of euhedral crystals; Kowarska Czuba Mt.

### Pyrargyrite $Ag_3SbS_3$

Introductory information about pyrargyrite may be found at the beginning of the section on proustite. The frequently used former name for pyrargyrite was *dunkles Rothgültigerz* (Jonas 1820, p. 374). The present name was proposed by Glocker (1831, p. 388). Recently, Laufek *et al.* (2010) discussed the position and influence of Ag in this mineral structure.

The mineral is trigonal, class ditrigonal pyramidal  $3m$ . The investigated specimen from Krowia Kopa Mt. has faces of pyramids and prisms and is essentially euhedral, but with window faces of the pyramids and slats on prisms parallel to the *C* axis (Text-



Text-fig. 14. Pyrargyrite, drawing of parallel growth of crystals; Krowia Kopa Mt.

fig. 14). This indicates unstable conditions during the final part of crystallization, such as decreasing inflow of the components to the growing crystal. The chemical composition is close to the pyrargyrite end-member of the proustite-pyrargyrite series (analysis no. 24 in Table 3) with 0.16 wt. % As replacing Sb, and 0.24 wt. % Cu and 0.46 wt. % Pb located in the Ag site. The S sites accepted 0.14 wt. % Te and 0.12 wt. % Se. Compositional zoning in the crystal was not observed, thus the changing inflow probably was not connected with variable proportions of the components. The calculated formula is  $(Ag_{2.97}Cu_{0.02}Pb_{0.01})_{\Sigma 3.00}(As_{0.01}Sb_{0.99})_{\Sigma 1.00}(S_{2.98}Se_{0.01}Te_{0.01})_{\Sigma 3.00}$ .

### Aguilarite $Ag_4SeS$

Aguilarite as a new mineral was recognized by Genth (1891, 1892) in samples sent to him from the San Carlos Mine at Guanajuato, Mexico<sup>2</sup>. This fairly uncommon mineral was found e.g., in the ores at Comstock Lode near Virginia City in Nevada, where it was “unsuspected” (Coats 1936, p. 532). Likewise, Main *et al.* (1972, p. 961) who described aguilarite from Camoola Reef at Silver Queen Mine,

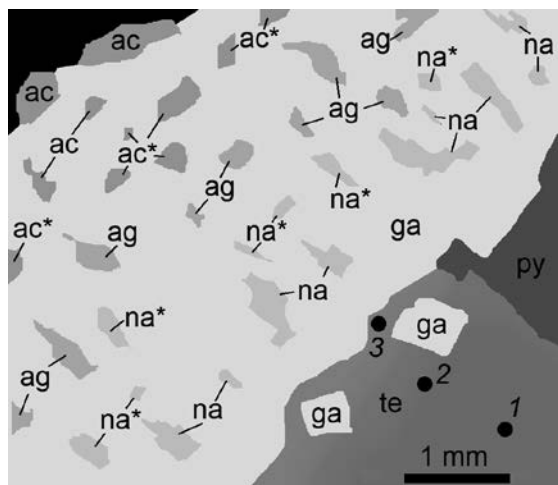
<sup>2</sup> A very interesting story connected with the life of Ponciano Aguilar who found the specimen of the mineral called later aguilarite was written by Elizabeth E. Ferry (2013).

Mineral / occurrence	No.	Ag	Au	Cu	Hg	Sn	Pb	As	Sb	Bi	S	Se	Te	Σ
Aguilarite														
Miedziane Skały Mt.	25	78.39		0.50	0.41						5.91	14.29	0.49	99.99
Cervelleite														
Popiel Mt.	28	70.53		0.84			0.74		0.37	0.32	5.28	0.69	21.18	99.95
Muthmannite														
Kowarska Czuba Mt.	29	18.78	33.68	0.61	0.58	0.27*			0.26		0.12	0.60	45.04	99.94
Naumannite														
Miedziane Skały Mt.	26	71.04		1.12			0.92	0.20			0.001	26.69		99.97
	27	69.96	1.21	1.34	0.55		0.78	0.23			0.56	25.33		99.96
Stützite														
Popiel Mt.	30	54.45	0.82	0.88			0.75		0.25	0.26	0.08	0.55	41.92	99.96
Tsnigriite														
Piaskowa Mt.	31	61.17		0.17	0.14	0.20		0.16	7.33	0.29	6.09	0.14	24.29	99.98
Volynskite														
Szklarska Poręba Huta	32	17.38	0.45	1.04		0.65	1.55	0.003	0.006	34.59	0.22	0.74	43.35	99.97

Table 4. Chemical composition of the silver selenides and tellurides, in wt. %; empty cells – component below detection limit (<~0.001 wt%).

Coromandel Peninsula, New Zealand, mentioned that it is “rare sulpho-selenide”. Vassallo (1988) published the precise investigations of aguilarite and other end members of this system, i.e., acanthite and naumannite, all from the ore deposit of the type region Guanajuato. The first X-ray diffraction studies of aguilarite from the type locality were made by Earley (1950) and a crystal structure model was presented by Bindi and Pingitore (2013).

Aguilarite is monoclinic (class – prismatic 2/m), however it may form pseudoisometric dendritic crystals. The specimen from Miedziane Skały Mt. contained this mineral as inclusions in galena (Text-fig. 15). The ore mineral assemblage started to crystallize from pyrite and tetrahedrite with galena



Text-fig. 15. Aguilarite (ag), naumannite (na), S-bearing naumannite (na\*), acanthite (ac) and Se-bearing acanthite (ac\*), galena (ga), pyrite (py) and tetrahedrite (te), 1–3 – analysed points in tetrahedrite, BSE image; Miedziane Skały Mt.

inclusions in the marginal part of a mineral of the tetrahedrite group. Next, galena became the main mineral with a zone of the naumannite inclusions. This naumannite contained only a trace of S, but deeper in the galena grain it became richer in this element and a zone with anhedral inclusions of aguilarite appeared (analysis no. 25 in Table 4). Close to the outer margin of galena, firstly Se-bearing acanthite (0.99 wt. %) inclusions were found, and in the outermost zone the acanthite inclusions were Se-free (analyses nos. 03 and 04 in Table 2). These data suggest that during crystallization of minerals of this association Se was present in the mineral-forming fluid, but next its concentration gradually decreased. Ag was found (in wt. %: point 1 – 0.04, point 2 – 0.11 and point 3 – 0.19) in the tetrahedrite-group mineral, and the values increasing towards the inclusions of the Ag minerals marked the appearance of this element in the parent solution.

Aguilarite in this association contains 0.50 wt. % Cu and 0.41 wt. % Hg that replaced silver. Sulphur is present in the theoretical amount, but selenium co-occurs with tellurium (0.49 wt. %) in the mineral structure; in other minerals of this association the latter element was not found. The calculated chemical formula of aguilarite is  $(\text{Ag}_{3.94}\text{Cu}_{0.04}\text{Hg}_{0.01})\Sigma_{3.99}\text{S}_{1.00}(\text{Se}_{0.98}\text{Te}_{0.02})\Sigma_{1.00}$ .

#### Naumannite $\text{Ag}_2\text{Se}$

This mineral was first described from the Tilkeroode deposit in the Harz Mts., Germany, as *Selen-Silber* (Rose 1828, 1830) and the present name was given by Haidinger (1845, p. 565). It is not rare in silver deposits containing Se (see e.g., Davidson

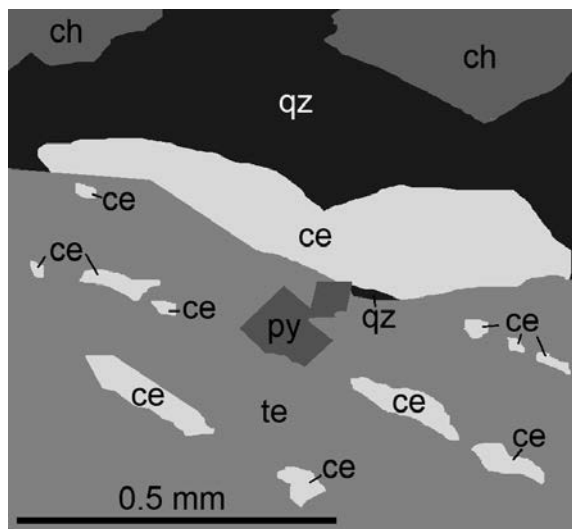
1960; Frigstad 1972; Škácha *et al.* 2017; Pažout *et al.* 2019). It was also synthesized (Earley 1950) and the properties of its crystals, structure inclusively, were characterized (Wiegner 1971; Yu and Yun 2011).

Naumannite occurrence in the form of crystal inclusions in a galena grain in the sample from Miedziane Skały Mt. was described above. Its structure is orthorhombic (disphenoidal, class 222); the investigated grains, however, were anhedral (Text-fig. 15). The chemical composition (analyses nos. 26 and 27 in Table 4) of the S-poor variety includes (in wt. %) 1.12 Cu, 0.92 Pb and 0.20 As, and its formula is  $(\text{Ag}_{1.93}\text{Cu}_{0.05}\text{Pb}_{0.01})_{\Sigma 1.99}(\text{Se}_{0.99}\text{As}_{0.01})_{\Sigma 1.00}$ . The grains with an admixture of 0.56 wt. % S have also 1.21 Au, 1.34 Cu, 0.55 Pb 0.78 Pb and 0.23 As (in wt. %), thus  $(\text{Ag}_{1.90}\text{Cu}_{0.06}\text{Au}_{0.02}\text{Hg}_{0.01}\text{Pb}_{0.01})_{\Sigma 2.00}(\text{Se}_{0.94}\text{S}_{0.05}\text{As}_{0.01})_{\Sigma 1.00}$  is the proposed formula.

### Cervelleite $\text{Ag}_4\text{TeS}$

This telluride was first found in the abandoned Bambolla mine near Moctezuma in Sonora, Mexico (Criddle *et al.* 1989). Soon after it was sought in other deposits (cf. Helmy 1999) and has been found, albeit infrequently (e.g., Mugas Lobos *et al.* 2012; Pujol *et al.* 2012; Kubač *et al.* 2018). A study of its structure was published by Bindi *et al.* (2015).

Cervelleite crystals are monoclinic (class 2/m, prismatic). However, the specimen found at Popiel Mt. contains anhedral grains (one seemingly subhedral) on and in a mineral of the tetrahedrite group (Text-fig. 16). The inclusions are arranged along the



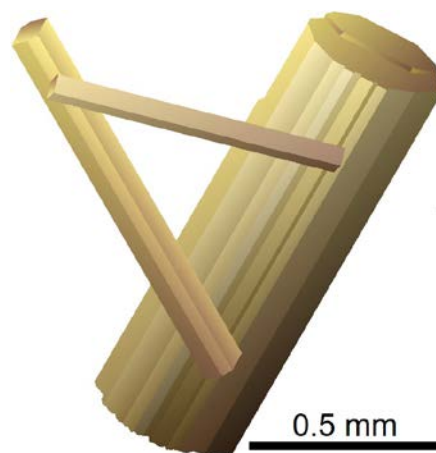
Text-fig. 16. Cervelleite (ce) as inclusions in a tetrahedrite (te) grain and on its surface, ch – chalcopyrite, py – pyrite, qz – quartz, BSE image; Popiel Mt.

growth zones of the host mineral, thus these two minerals form a paragenesis. Pyrite and chalcopyrite are neighbouring minerals. The chemical composition of cervelleite is typical (analysis no. 28 in Table 4) with admixtures (in wt. %) of Cu (0.89), Pb (0.74), Sb (0.37), Bi (0.32) and Se (0.69), thus  $(\text{Ag}_{3.86}\text{Cu}_{0.08}\text{Pb}_{0.02}\text{Sb}_{0.02}\text{Bi}_{0.01})_{\Sigma 3.99}(\text{Te}_{0.98}\text{S}_{0.97}\text{Se}_{0.05})_{\Sigma 2.00}$  is the mineral formula.

### Muthmannite $\text{AuAgTe}_2$

The first known occurrence of muthmannite was recognized by Zambonini (1911) in a specimen from the Săcărâmb open pit mine of Au, Se and Te ore (Hunedoara region, Romania). A comprehensive study of muthmannite from this deposit was made by Bindi and Cipriani (2004). Boyle (1968, p. 21) wrote that muthmannite is a common mineral in the telluride assemblage at Nagyág (i.e., Săcărâmb), Romania, but has not been recorded in Canadian deposits. In fact this mineral is not common and has even been termed “exceptionally rare” (Cook 2001, p. 8). Such an exceptional occurrence was applied to the Sakkati Ni-Cu-PGE deposit in Finland (Fröhlich *et al.* 2021, p. 1504).

Muthmannite forms monoclinic crystals (prismatic class 2/m). The specimen found at Kowarska Czuba Mt. was c. 1.5 mm in size and consisted of three crystals of prismatic habit (Text-fig. 17). The two smaller were single and the largest was a parallel growth of two (or more) crystals with striation along the C axis. Its colour was yellow with a brown-greyish tint. The chemical composition of all three crystals was the same and no zoning was found. Cu (0.61 wt. %), Hg (0.58 wt. %), Fe (0.27 wt. %), Sb (0.26 wt. %) and Se (0.60 wt.



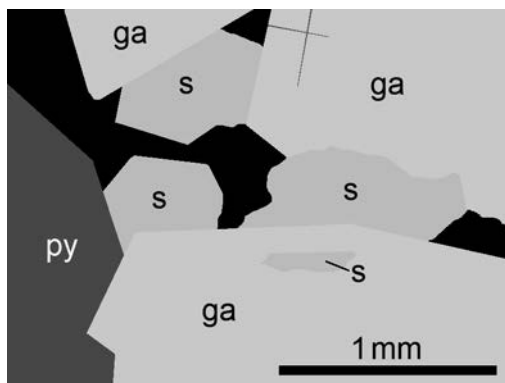
Text-fig. 17. Muthmannite, drawing of growth of three euhedral crystals; Kowarska Czuba Mt.

%) were the minor elements (analysis No. 29 in Table 4) and  $(\text{Ag}_{0.96}\text{Au}_{0.94}\text{Cu}_{0.05}\text{Fe}_{0.03}\text{Hg}_{0.02}\text{Sb}_{0.01})_{\Sigma 2.01}(\text{Te}_{1.94}\text{Se}_{0.04}\text{S}_{0.02})_{\Sigma 2.00}$  is the calculated formula. The presence of Au in the chemical composition of these crystals can be associated with the occurrence of native gold as ‘micromineral’ specimens in the Karkonosze pluton (Kozłowski 2011).

### Stützite $\text{Ag}_{5-x}\text{Te}_3$

*Tellursilberblende* (Petz 1842) was the early name of the Ag-Te group of minerals; that investigated by Schrauf (1878a, b) was named by him as stützite; the specimen was collected at Săcărâmb mine in the Hunedoara region, Romania. Stützite was found in numerous locations and many of its occurrences were very well investigated, e.g., those in Romania (Apopei *et al.* 2014), but also e.g., in Africa (Wille 2004) and Asia (Jingwen *et al.* 1995). Likewise, its structure was interesting for mineralogists (Bayliss 1990; Bindi and Keutsch 2017), especially in connection with the phase equilibria of the Ag-Au-Te system (e.g., Honea 1964).

Stützite from Popiel Mt. occurs associated with pyrite and in paragenesis with galena. Crystals of this telluride (up to 1 mm in size) have subhedral habit, and occur between galena grains and as inclusions in them (Text-fig. 18). One crystal has a hexagonal outline that refers to two trigonal prisms of the class of trigonal dipyramid  $\bar{6}$  (hexagonal system). The chemical composition of these stützite grains shows minor elements (in wt. %): Au – 0.82, Cu – 0.88, Pb – 0.75, Sb – 0.25, Bi – 0.26 and Se – 0.55 (analysis no. 30 in Table 4). Neither crystal zoning nor differences in composition between the grains were found. Together with the main components it resulted in the formula:  $(\text{Ag}_{4.49}\text{Au}_{0.04}\text{Cu}_{0.13}\text{Pb}_{0.03}\text{Sb}_{0.02}\text{Bi}_{0.01})_{\Sigma 4.72}(\text{Te}_{2.92}\text{Se}_{0.06}\text{S}_{0.02})_{\Sigma 3.00}$ .

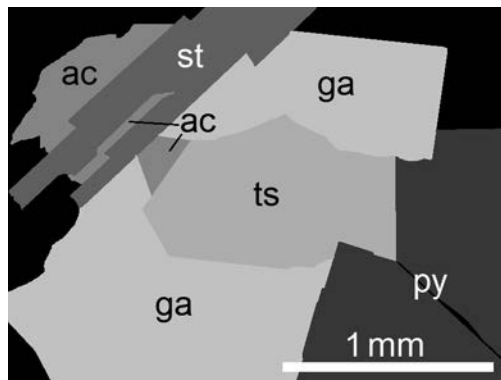


Text-fig. 18. Stützite (s) with galena (ga) and pyrite (py), black – quartz, BSE image; Popiel Mt.

### Tsnigriite $\text{Ag}_9\text{SbTe}_3(\text{S},\text{Se})_3$

This mineral was recognized as new in the ore of the Au-Ag Vysokovoľt'noe deposit in the western part of the Southern Tyanshan area, Uzbekistan, and next found in the polymetallic Bethumi deposit in Rajasthan, India (Sandomirskaya *et al.* 1992). Later, tsnigriite was identified in a few locations in Russia, e.g., eastern Yakutia (Anisimova and Kondrat'eva 2012), and in Austria (Paar and Putz 2018). Cook (2001, p. 15) classified the occurrence of tsnigriite as “exceptionally rare”.

Tsnigriite crystallizes in the monoclinic system, prismatic class 2/m. In the specimen from Piaskowa Mt. only one c. 1 mm long grain of tsnigriite was found. It has a habit which may be named as subhedral. This grain occurs between crystals of galena, pyrite and acanthite; closely also occurs a stromeyerite crystal (Text-fig. 19). The chemical composition of the tsnigriite crystal was uniform, with minor components (in wt. %): Cu – 0.17, Hg – 0.14, Sn – 0.20, As – 0.16, Bi – 0.29, and Se – 0.14. The chemical formula, calculated on the basis of analysis no. 31 (Table 4) is  $(\text{Ag}_{8.91}\text{Cu}_{0.04}\text{Sn}_{0.03}\text{Hg}_{0.01})_{\Sigma 8.99}(\text{Sb}_{0.95}\text{As}_{0.03}\text{Bi}_{0.02})_{\Sigma 1.00}(\text{Te}_{2.99}\text{S}_{2.98}\text{Se}_{0.03})_{\Sigma 6.00}$ . The chemical composition of stromeyerite from this specimen is given above as analysis no. 17 (Table 2); acanthite was not determined quantitatively.

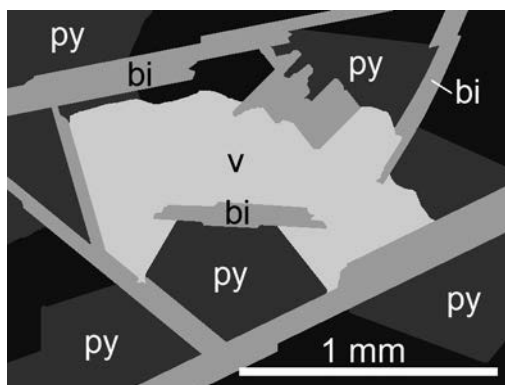


Text-fig. 19. Tsnigriite (ts), stromeyerite (st), acanthite (ac), galena (ga), pyrite (py), black – quartz, BSE image; Piaskowa Mt.

### Volynskite $\text{AgBiTe}_2$

Volynskite was recognized as a new mineral in the Zod Mine, Sotk deposit near Vardenis in Gegharkunik Province, Armenia by Bezsmertnaya and Soboleva (1965). Since that time it has been found in many deposits with Ag-Te mineralization. Good examples are, e.g., the Ashley deposit in Ontario,





Text-fig. 20. Volynskite (v), bismuthinite (bi), pyrite (py), black – quartz, BSE image; Szklarska Poręba Huta.

Canada (Harris *et al.* 1983), the Yangzhaiyu gold deposit in the Xiaoqinling region, central China (Jian *et al.* 2014), or skarns at Ocna de Fier in Dognecea, Romania (Cook and Ciobanu 2001)

Volynskite is a trigonal mineral in the ditrigonal scalenohedral  $\bar{3}2m$  class, but in the specimen collected at Szklarska Poręba Huta it is a c. 1.5 mm long anhedral grain, surrounded by subhedral grains of pyrite and laths of bismuthinite (Text-fig. 20). It has minor admixtures of the elements (in wt. %): Au – 0.45, Cu – 1.04, Sn – 0.65, Pb – 1.55, As – ~0.01, Sb – ~0.01, S – 0.22, and Se – 0.74 (analysis no. 32 in Table 4). Neither the main nor minor components displayed zoning. The whole analytical data yield the formula:  $(Ag_{0.91}Cu_{0.09}Au_{0.01})_{\Sigma 1.01}(Bi_{0.93}Pb_{0.04}Sn_{0.03})_{\Sigma 1.00}(Te_{1.91}Se_{0.05}S_{0.04})_{\Sigma 2.00}$ .

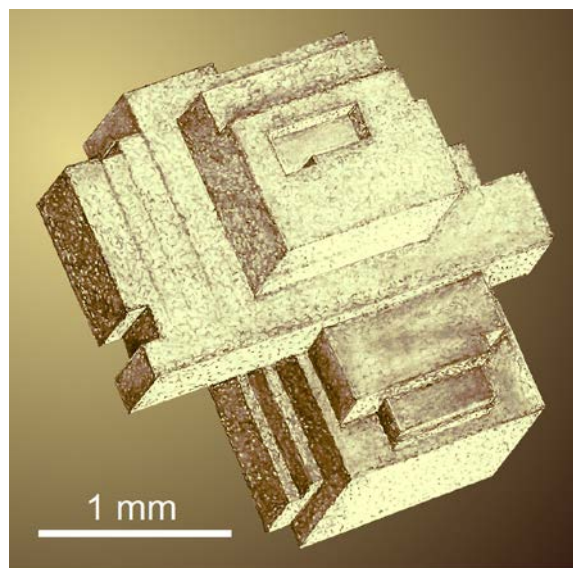
### Chlorargyrite AgCl

This mineral as a component of silver ores was named *Hornsilber* or *Hornerz* in the past (Agricola 1558). Gesnerus (1565, p. 62) described chlorargyrite as: *Flavi coloris (...) Cornu pellucido simile, Mariebergium: candela admotum liquescit. Ein durchsichtig hornfarbs gedigen silber / das am lichte verschmiltzt.* (In Latin: Yellow colours. Similar to transparent horn, Marienberg: placed close to a candle melts. In German: Translucent horn-coloured true silver, which melts in flames; Marienberg is a town in the Erzgebirge near the silver ore mines, accepted as the type locality of chlorargyrite). The early name evolved to cerargyrite (Breithaupt 1841, pp. 315–317) and then to the present one which was promoted by Weisbach (1875, p. 37).

Chlorargyrite forms usually in a hypergenic environment, especially in a dry climate, in the presence

of chloride ions as in the Chloride area in Arizona (Bastin 1925) or in the deposits of Dzungar Alatau, Kazakhstan (Umarbekova *et al.* 2020). However, these ions may appear from the buried waters of a marine palaeobasin, as in the Corrida deposit in the Chukchi Peninsula, Russia (Kolova *et al.* 2021), thus this mineral may not necessarily crystallize under surface conditions.

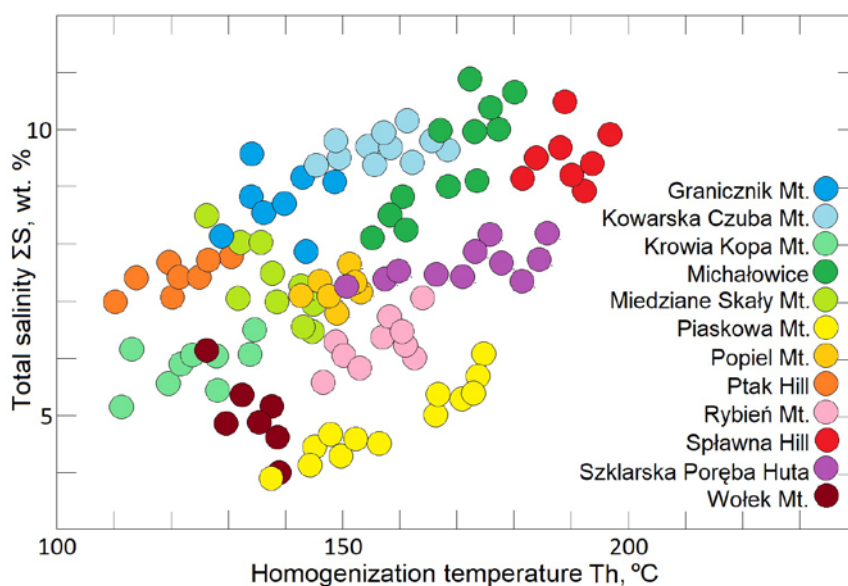
Chlorargyrite crystallizes in the isometric system, hexoctahedral class  $m\bar{3}m$  (Prior and Spencer 1902) and the crystals are cubic, but this habit is rare. Most commonly it forms dense clots or encrustations. The specimen from Cicha Równia Mt. is a c. 3 mm large group of cubic-type parallel grown crystals of elongated and flattened habits with the window face (Text-fig. 21). The specimen is translucent and of pale yellow colour with brownish fine-grained coating. It occurred with pyrite, arsenopyrite (both corroded), hematite and goethite; no Ag minerals other than chlorargyrite were found there. Minor amounts of Cu, Br and I were found in the chemical composition of chlorargyrite, which is as follows: Ag – 73.55, Cu – 0.48, Cl – 23.49, Br – 1.77, I – 0.70,  $\Sigma 99.99$  wt. %. This yields the formula  $(Ag_{0.99}Cu_{0.01})_{\Sigma 1.00}(Cl_{0.96}Br_{0.03}I_{0.01})_{\Sigma 1.00}$ . The contents of Br and I are low and fit to the chlorargyrite structure (cf. e.g., Gillard *et al.* 1997). Corrosion of pyrite and arsenopyrite indicates the activity of late fluids, not connected with the crystallization of sulphides, and the absence of a primary Ag mineral may suggest its complete alteration to chlorargyrite. The almost perfect habit of chlorar-



Text-fig. 21. Chlorargyrite, drawing of a parallel growth of crystals with elongated or flattened cubic habits, one face of the window type; Cicha Równia Mt.

Occurrences	<i>N</i>	Th [°C]	ΣS [wt. %]	Na <sub>2</sub> CO <sub>3</sub> [wt. %]	Ca(HCO <sub>3</sub> ) <sub>2</sub> [wt. %]
Granicznik Mt.	8	128–148	7.9–9.6	6.0–7.7	1.1–1.4
Kowska Czuba Mt.	11	145–168	9.5–10.1	8.1–8.8	1.2–1.3
Krowia Kopa Mt.	9	112–135	5.3–6.5	4.6–5.8	0.6–0.7
Michałowice	12	155–180	8.0–10.8	7.2–9.9	0.7–0.9
Miedziane Skąły Mt.	10	126–146	6.4–8.5	5.9–7.8	0.5–0.8
Piaskowa Mt.	13	138–175	3.9–6.0	3.3–7.1	0.5–0.7
Popiel Mt.	7	143–154	6.8–7.6	6.1–6.8	0.6–0.8
Ptak Hill	8	109–133	7.0–7.8	6.0–6.7	0.9–1.2
Rybień Mt.	10	147–164	5.5–7.0	4.9–6.4	0.6–0.7
Splawna Hill	8	182–197	8.9–10.4	8.0–8.3	0.9–1.2
Szklarska Poręba Huta	11	150–186	7.2–8.1	6.5–7.5	0.6–0.8
Wolek Mt.	7	126–139	4.0–5.2	3.5–4.6	0.4–0.6

Table 5. Ranges of homogenization temperature (Th), total salinity (ΣS), and concentrations of the main dissolved components in primary inclusion fluids in quartz from mineral associations with silver compounds; *N* – number of inclusions. Note: chlorargyrite at Cicha Równia Mt. formed from a low-temperature hypergenic fluid and inclusions related to its origin were not found.



Text-fig. 22. Plot of homogenization temperature vs. total salinity for fluid inclusions in quartz from the mineral associations with silver compounds.

gyrite formed probably during slow and quiet crystallization and the window face appeared due to the exhaustion of Ag in the parent fluid.

### Galena and tetrahedrite-group minerals

It should be mentioned that Ag was also a minor component of galena and a mineral of the tetrahedrite group in the mineral associations described above. Nevertheless, because the Ag amounts are low (0.08–0.15 wt. % in galena and 0.06–0.11 wt. % in the tetrahedrite-group mineral), these two are not considered here as silver minerals.

### Fluid inclusions

Fluid inclusions, which were appropriate for the investigation, occurred in quartz, the main gangue mineral of the studied samples. However, only a few of the silver minerals occurred in or close to quartz, others were separated by associated sulphides, etc., or only in small parts were surrounded by quartz and their main portions were not overgrown at all. Moreover, quartz close to the silver minerals was usually free of inclusions due to stable conditions of slow crystallization. Therefore the inclusion data refer to the conditions of the silver minerals origin

only approximately, though the inaccuracy should not be significant.

The size of the inclusions did not exceed c. 10  $\mu\text{m}$ . Their filling at room temperature was two phase aqueous, but on cooling at c. +4 to +2°C, a thin rim of liquid  $\text{CO}_2$  appeared around the gas bubble. Neither trapped nor daughter minerals were found. Generally, the Th values ranged from 112 to 197°C and the total salinity – from 3.9 to 10.8 wt. % (Table 5 and Text-fig. 22). Sodium carbonate and calcium bicarbonate were the main components with a distinct dominance of the first. As minor components, Cl, F, S, K, Fe and Al were found with probable concentrations of a few tenths of a percent. Carbon dioxide was also a common though subordinate ingredient of the mineral-forming fluid. Despite the presence of  $\text{CO}_2$  in the inclusions, a determination of pressure was not possible.

The total set of the points Th/ $\Sigma\text{S}$  is in an oval field with the longer axis according to the 'greater Th – greater  $\Sigma\text{S}$ ' values. Some of the data from individual samples have the same distribution but they may form nearly isometric fields or even display the 'greater Th – smaller  $\Sigma\text{S}$ ' relationship (Text-fig. 22). Thus, although the crystallization of the silver compounds in this granitoid is a kind of overall process, as suggested by the general composition of the mineral-forming fluids, some details depend on local factors like the rate of temperature change, mechanical tension development, mode of fissure opening, etc.

## DISCUSSION

Silver mineralization was found in areas adjacent to the Karkonosze pluton (cf. publications cited in the introduction and references therein) and ores of this metal were exploited in the rocks of the metamorphic envelope of the pluton, e.g., in its eastern part at Miedzianka–Ciechanowice (Websky 1853; Birnbaum 1891) and in the southern one, e.g., at Černý Důl or at Svatý Petr in Špindlerův Mlýn (Jokely 1862). Moreover, minerals of As and Bi (Gołębiewska 1999; Siuda *et al.* 2010), Se (Mochnacka 1971; Parafiniuk 2008), Te (Parafiniuk 2003; Gołębiewska *et al.* 2011; Pieczka *et al.* 2011; Rybicki 2012) and minerals of other elements that also are components of the studied silver compounds, occur in the envelope rocks. Thus the idea of a direct relationship between the envelope and the silver minerals in the batholith would be a most obvious model. But the way(s) in which these elements (i.e., Ag, As, S etc.) migrated either to or from the

batholith have not yet been found. Generally, such migration is probably possible, as suggested by the investigations of F and Li presence in the quartz of the silicification zone of Izerskie Garby close to the northern contact of the Karkonosze batholith with its envelope (Kozłowski and Metz 2004). The results of other studies of the Li content in the rock-forming quartz of the Karkonosze granitoid and its northern envelope rocks would suggest that this element could migrate from the granitoid to the envelope schist of gneiss (Kozłowski 2002b). Similar migration would perhaps be possible for other elements, not only from magma but from the metamorphic envelope into the melt reservoir as well. Another possibility is that the intruding magma mingled with melted envelope rocks and this process resulted e.g., in a small inflow of the components of the considered minerals (Ag, Au, Cu, Pb, Hg, Zn, Sn, As, Sb, Bi, S, Se, Te) to the granitoid, but checking this supposition would require thorough geochemical studies of trace elements in large areas of the granitoid and envelope rocks.

A different scheme is possible. Granitoid of the pluton was subjected to the activity of local post-magmatic fluids which caused partial alteration of the magmatic minerals, e.g., albitization of oligoclase (Nowakowski and Kozłowski 1981) and muscovitization or chloritization of biotite. This process could be connected with mobilization of trace elements. The Karkonosze granitoid contains c. 0.05 ppm Ag as trace element (authors' data from 5 samples: from 0.039 to 0.056 ppm), which is similar to the contents in other granitoids, e.g., those published by Hamaguchi and Kuroda (1959). If 1 mg Ag is in a 'micromineral', such amount is present in the granitoid cube with an edge of 20 cm. Of course, not all silver would be 'washed out' from the rock, but even if 10% of it could be mobilized, the rock volume is not large. Also other trace elements may become mobile this way and next migrate to the crystallization nucleus.

Another argument for this source of the components of the studied minerals is as follows: the size of the minerals is very small, their crystallization was slow and quiet, their compositions (thus the available elements) are different for particular locations and the parameters and evolution of the parent fluids were different in each case. Thus it was not a general process but local 'spotty' events in quite propitious but small-scale conditions. As for silver, the presence of fluoride ions in the fluid caused its good mobility, because  $\text{AgF}$  is well soluble.

These events appeared as final ones in the evolution of the fluids in the Karkonosze pluton. The car-

bonate-rich fluid is similar to the present-day thermal waters in the Karkonosze pluton (cf. e.g., Fistek and Fistek 2005, and the discussion in Kozłowski and Matyszczyk 2022, and the references therein).

## CONCLUSIONS

Twenty silver sulphides, arsenides, selenides, tellurides, sulphosalts and chloride were found in the Karkonosze granitoid pluton as the minerals: aguilrite, acanthite, argentite, argyrodite, balkanite, canfieldite, cervelleite, chlorargyrite, freieslebenite, matildite, muthmannite, naumannite, novákite, owyheeite, proustite, pyrrargyrite, stromeyerite, stützite, tsnigriite and volynskite. They occurred in quartz veins and in pegmatites in 13 localities. No alteration of these minerals was found except for the paramorphic replacement of argentite by acanthite.

The X-ray diffraction data and chemical compositions are typical of the phases, and the trace elements abundances are rather low. Different concentrations of Cu in post-argentite acanthite and in primary acanthite, and easier etching of the paramorphs in acid solutions allowed us to distinguish the former presence of these two structural varieties of  $\text{Ag}_2\text{S}$ .

The minerals formed from epithermal fluids; only chlorargyrite probably crystallized from a supergene solution. The values of the two-phase inclusions in quartz associated with the silver minerals ranged from 112 to 197°C and the total salinity – from 3.9 to 10.8 wt. %. Na and Ca carbonates were the main dissolved substances; Cl, F, S, K, Fe and Al are the minor components. The very low abundance of  $\text{CO}_2$  was common. The fluid composition is similar to that of the present-day thermal waters of the Karkonosze pluton.

Most probably Ag and other components that formed the minerals were from very local sources – from trace elements from a small volume of the pluton granitoid, which were released to the epithermal solution during post-magmatic alteration of the host rock minerals. Ways of migration of the parent fluids of the Ag minerals to the studied occurrences from the Ag mineralization zones in the pluton envelope or inside the pluton were not found.

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