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Minerals of antimony: a newly found occurrence in the Karkonosze granitoid pluton and a review for Lower Silesia, Poland, with general background

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ABSTRACT:

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The article describes assemblages of ore minerals of the size of tenths to a few millimetres, which occurred in small quartz veinlets and nests in 10 previously unknown sites. This mineralization was found in the north-eastern part of the Karkonosze granitoid pluton at the southern slope of the Wysoki Grzbiet (High Ridge) in Izera Mts. The studies concerned mainly 18 Sb minerals: antimony, Sb-bearing domeykite, getchellite, stibnite, willyamite, berthierite, boulangerite, bournonite, chalcostibite, falkmanite, famatinite, geocronite, robinsonite, semseyite, tetrahedrite-(Fe), cervantite, kermesite and schafarzikite; seven of them have been found in Poland for the first time. The parageneses, morphological features, XRD data and chemical composition of the Sb minerals are presented. Fluid inclusions in quartz adhering to the Sb minerals had generally homogenization temperature (Th) 108–341°C and total salinity ΣS 4.6–10.1 wt. %. The inclusion fluids were of the $NaCO_3$-$Ca(HCO_3)_2$-NaCl-KCl type with minor F and S, and occasional CO_2 presence. The parent granitoid contains Sb in trace amounts (0.18–0.36 ppm) and the rock was possibly a source of this (and other) element(s) for the ore minerals. Migration of meso-epithermal solutions with Sb etc. was probably stimulated by local reduction of pressure during the formation of fissures and cracks in granite, next filled by quartz with ore minerals. The features of the historical process of the recognition of Sb ores and previous studies of the minerals investigated in this research are included in the presentation and discussion. Special attention was paid to the listing of the occurreences of Sb minerals in Lower Silesia with appropriate references.

Key words: Sb minerals; Fluid inclusions; Granitoid; Karkonosze pluton, Lower Silesia.

Motto: *Let's remember the words of our predecessors in science.*

GENERAL INTRODUCTION

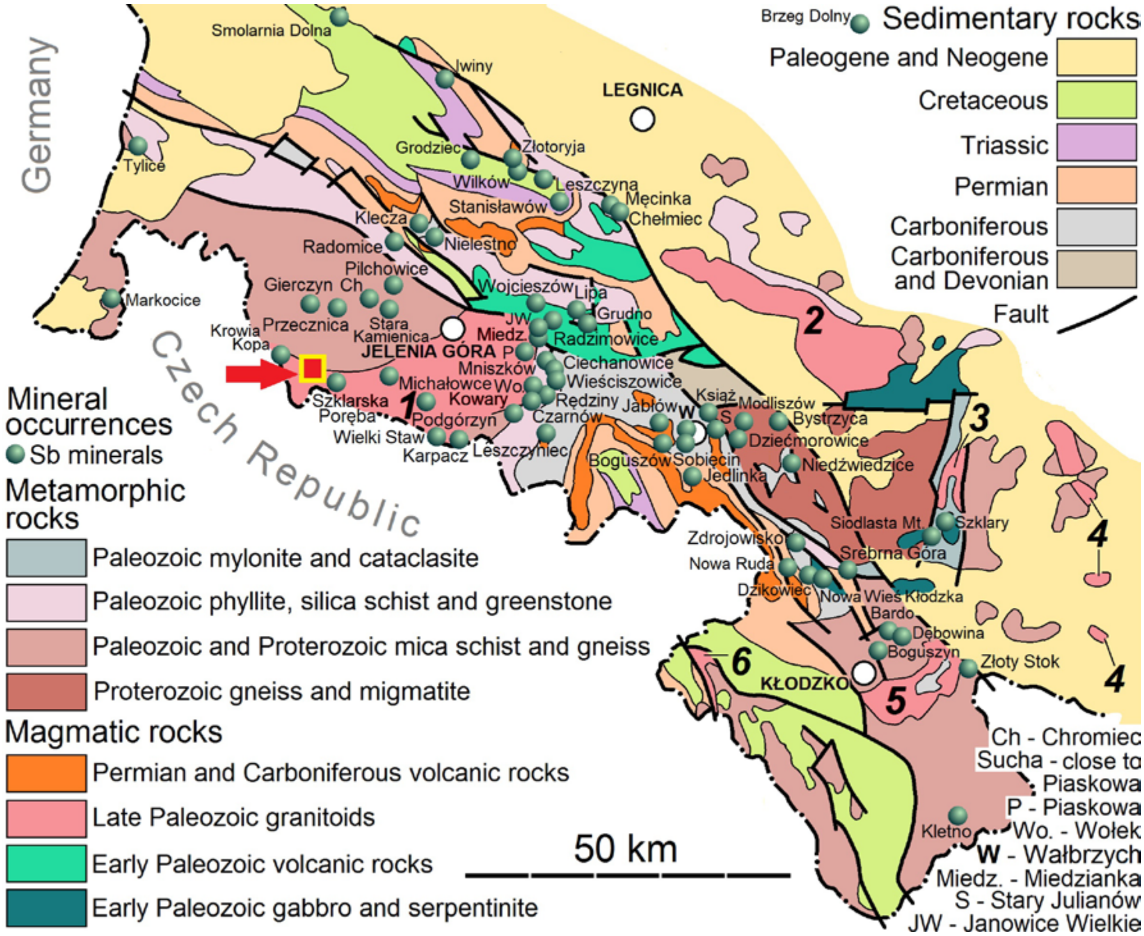
Already in 5500–3300 BCE (Chalcolitic age) antimony minerals became in the Near East region an important component of ores for the production of copper alloys containing 1 to 20 wt. % Sb (Dillis *et al.* 2019). Also later in the Early Bronze age (since 3100 BCE) Sb remained a significant part (c. 2 to 14 wt. %) of copper-tin alloys i.e. bronzes of various kind (Dardeniz 2020). Moreover, it was used as an opacifier and decolouriser of glass (Dillis *et al.* 2019) or for the preparation of cosmetics called by the Sumerians *šimzida* and *šimbizi* (Civil and Foxvog 2009). Theofrastos (c. 370–287 BCE) supposedly used the Greek name *ανθραξι* (*anthraksi*; Theofrastos 1975, p. 19 paragraph 39) for a group of mineral substances that included Ag-Sb sulphide ore. Plinius (23–79 CE) described (see e.g. 1857, pp. 115, 116) the ancient use of powdered antimony and stibnite named *stimmi*, *stibi* and *platyophthalmon* as medicines and cosmetics for eyes. A probable erroneous Medieval description (Albertus Magnus 1270) of Sb (and Bi) minerals as Sn ores was discussed by Prof. Dorothy Wyckoff in comments made in a part of the modern Albertus Magnus book issue (1967). Agricola (1561) presented Sb minerals (*lapide ſtibio*, *ſpiſglas*) and its use mainly as an ore in metallurgy. The very interesting and logically arranged book prepared by Albinus (1590) contains a section on Sb minerals (pp. 137–138). The author listed the names used for Sb and (or) its ores: *stibi, ςίμμμι* (*simmi*), *Spießglas*, *Spißglantz*, *Glaßerts*, *Glantzertz*; the Latin term *plumbum nigrum* (black lead) could be the source of the later name *Schwarzspiesglaßerz* used for Pb-Sb-Cu-S ore (Bonnard 1815). Such a practical context stimulated mineralogical studies and resulted in better listing of the characteristics of the Sb compounds, like that one published by Becher (1661, pp. 107–125). Schvvenckfelt (1600, p. 393) and Kretschmar (1662, chapter 13) prepared concise and clear descriptions of use of the Sb-containing substances as medicines, but only with general information that the Sb minerals (*antimonium*, *stibium*, *simmi*, *sibi*, *stibij vitrum*, *stibium hyalinum*, *Spießglas*, *Spießglantz*) occur in Lower Silesia, especially in Montes Gigantei (Karkonosze and Izera Mts.), notwithstanding without more exact locations. However, at that time natural history research was commonly in close contact with alchemy and substances containing Sb were considered to be very important in this field. A typical example presented several books of Valentinus's authorship (e.g. 1676), probably a fictitious person created, like the books, by Johann Thölden (cf. Prinke 2014, pp. 482–490, Breuning and Geist 2018, pp. 29–33). But a realistic approach developed as well, also in studies in Lower Silesia, as may be found e.g. in Volkmann's publication (1720, chapter VIII). It is worth noting that a good general description of the Sb minerals and their use was written by Kluk (1802).

So far the following 32 Sb minerals have been identified in Lower Silesia: andorite-IV, aramayoite, berthierite, bindheimite, boulangerite, bournonite, costibite, famatinite, freieslebenite, geocronite, giessenite, izoklakeite, jamesonite, kobellite, Sb-bearing matildite, miargyrite, antimony, owyheeite, paradocrasite, plagionite, polybasite, pyrargyrite, stephanite, stibiocolumbite, stibiconite, stibnite, tetrahedrite (group, including freibergite subgroup), tsnigriite, ullmannite, Sb-bearing volynskite, willyamite, zoubekite. They have been found in at least 65 locations (Text-fig. 1) – though the Legnica-Głogów Copper Ore District (see Oszczepalski 2007) was not included in this review. For more data and for appropriate references see Appendix 1. In the past a part of these locations was of industrial importance. But the previously unknown occurrence of the Sb "microminerals" in the endocontact zone of the Karkonosze pluton presented in this article is rather only of scientific meaning.

GEOLOGICAL SETTING

The Lower Silesian domain with the Karkonosze pluton as one of its components is the NE part of the Variscan Bohemian massif (Mazur *et al.* 2018). The massif is a result of the accumulation of the Neoproterozoic Gondwana continent fragments, gneiss blocks formed from Early Palaeozoic granitoid protoliths, areas of Middle Palaeozoic sediments from the margins of continents and basin series with ophiolite parts, Carboniferous granitoid plutons and rock assemblages of intramontane basins (Mazur *et al.* 2007). During the collisions of the tectonic segments whilst their accretion, intrusions and faults of various scale developed due to orogenic processes, Alpine ones inclusively, and they caused the blocky or "spotty" pattern of the arrangement of the rock series in Lower Silesia, including the Karkonosze pluton (Quenardel *et al.* 1988; Mazur *et al.* 2010), as it is visible in the geological map of this area (Text-fig. 1). The pluton is in contact with a metamorphic cover. On the north the cover consists of Early Palaeozoic gneiss and mica-chlorite and amphibolite schists with hornfels, metamafites with limestone; rocks akin to these ones form the eastern and southern exocontact zone with local high-pressure (up to 10 kbar) schists (see e.g. Raumer 1813, Oberc 1961; Teisseyre 1971; Borkowska *et al.* 1980; Chaloupský *et al.* 1989; Mazur 2003; Żelaźniewicz *et al.* 2003; Mazur 2005; Mazur *et al.* 2007, 2010, 2018 and references therein).

The Karkonosze pluton (present exposure: W-E c. 70 km, N-S 8 to 20 km) is a Variscan batholith; its surface is developed into mountain ridges and intra-montane valleys which started to form at the end of the Alpine orogeny. The earliest mentions of it (Ferber 1774, Pallas 1778) were connected with descriptions of the Czech granitoids. More precise characteristics of the Silesian (Karkonosze inclusively) granite composition and the differences between



Text-fig. 1. Occurrences of Sb minerals in Lower Silesia on the simplified geological map with Quaternary rock formations omitted (after Grocholski 1989, modified); plutons: ***1*** – Karkonosze, ***2*** – Strzegom, ***3*** – Niemcza, ***4*** – Strzelin-Žulová, ***5*** – Kłodzko-Złoty Stok, ***6*** – Kudowa-Olešnice; for the list of minerals in these 65 occurrences and the related references vide Appendix. The red arrow points the area of occurrence of the samples studied in this research, see Text-fig. 2.

granite and gneiss were published by Gerhard (1779, pp. 45–50). The latter problem was also discussed by Kapf (1794, granite pp. 1–4, gneiss pp. 4–6). Haidinger (1787, p. 18) included granite from Szklarska Poręba, Karpacz and Śnieżka in the systematic description of the rocks and Buch (1798) characterized textural differences between equigranular and porphyritic granitoids in Karkonosze. A continuation of such studies was published by Rose (1842), who recognized varieties of the Karkonosze granitoids: one built of a fine-grained quartz-feldspar-mica groundmass with dispersed several-centimeter long orthoclase porphyrocrysts, and next an equigranular medium-grained one with typical granitoid composition, and a very fine-grained granite-type rock with abundant albite, thus an aplitic variety frequently but not always forming veins. This description of the characteristics was completed in petrographic details by Klockmann (1882). The next review of the Karkonosze granitoid varieties with his own observations on the forms of occurrence was prepared by Berg (1923). Borkowska (1966) published an exact petrographic description of the pluton rocks; she used the names: central granite (earlier porphyritic granite), ridge granite (equigranular one) and granophyric granite (fine grained one). The QAPF system (Le Maître *et al.* 2002) applied to the Karkonosze granitoids indicated that the rock types called central and crest granite are in fact monzogranite and granodiorite (any of them may form parts of the central or crest ones), whereas the granophyric type is monzogranite only.

Investigations of melt inclusions in the magmatic quartz of the pluton provides evidence that the Karkonosze granitoid formed at 990 to 840°C from a melt of tonalitic to granitic composition (Kozłowski and Słaby 2004; Kozłowski 2007). There are some features suggesting that the melt went through a stage of mixing or mingling of felsic and mafic components of different origin (Słaby and Martin 2008). Most probably the formation of the intrusion was polyphase (Cloos 1924; Žák and Klomínský 2007; Žák *et al.* 2013, 2014; Klomínský 2018). The melt(s) intruded during the Late Carboniferous c. 312–315 Ma ago (Machowiak and Armstrong 2007; Žák *et al.* 2013; Kryza *et al.* 2014a, b; Kusiak *et al.* 2014; Mikulski *et al.* 2020).

SAMPLE OUTCROPS

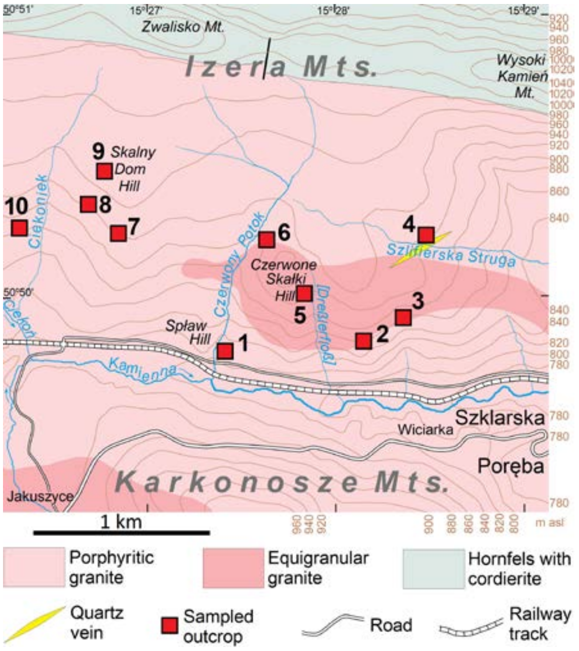
The investigated samples with Sb minerals were collected from quartz veinlets and nests in the porphyritic or equigranular granite of the Karkonosze pluton in the southern slope of the Wysoki Grzbiet (High Ridge) all the way to the Kamienna River left bank (Text-fig. 2). Although this area is built of Karkonosze pluton, geographically it is included in the Izera Mts. (Staffa *et al.* 1989). Post-magmatic quartz veins, veinlets and nests of various size are common in the Karkonosze pluton (Kozłowski 1973), also with ore minerals (Karwowski *et al.* 1973; Kozłowski *et al.* 1975). In the searched area the Sb minerals were found in ten outcrops (Text-fig. 2).

Outcrop 1, 15°27.47'E, 50°49.81'N. Small old quarry in porphyritic granite called Wiciarka 1 near the mouth of Czerwony Potok (Red Creek) to Kamienna River; vertical veinlet of gray quartz c. 1 cm thick, visible length 0.8 m, with ore minerals in two groups 2.7 and 3.4 cm long and up to 0.4 cm thick.

Outcrop 2. 15°28.15'E, 50°49.85'N. Place of former periodic exploitation of equigranular and porphyritic granite (Wiciarka 2), c. 0.25 km east of a streamlet now usually unnamed, rarely informally called Strużka i.e. Trickle, its old name was Dreßlerfluß* (Berg 1925); small irregular nest of whitish quartz 12 cm long with three 0.6–1 cm spots of ore minerals.

Outcrop 3. 15°28.34'E, 50°49.93'N. Small rock of equigranutar granite c. 2 m high, 0.15 km north of the source of an unnamed creek and 0.5 km east of Strużka (Dreßlerfluß) streamlet; vertical veinlet of light gray quartz 0.8–1.5 cm thick, visible length 1.2 m, with four streaks of ore minerals c. 2 cm long.

Outcrop 4. 15°28.49'E, 50°50.57'N. Small veinlet of grayish quartz 2–2.5 cm thick in the porphyritic granite with a streak of ore minerals 0.5×3 cm, 30 m NW from vein-type silicified zone of milky quartz approximately 300 m long in the Szlifierska Struga (stream) bed, 0.9 km ENE of the Czerwone Skałki (Red Rocks) Hill.



Text-fig. 2. Locations of the sample collecting, southern slope of Izera Mts. west of Szklarska Poręba, geological background after Berg (1925); note – Spław Hill near to this outcrop is sometimes called Spławna Hill.

Outcrop 5. 15°27.83'E, 50°50.01'N. Small wall of the equigranular granite c. 50 m SE of the top of Czerwone Skałki Hill; oval nest of dark gray quartz c. 11 cm long with dispersed ore minerals.

Outcrop 6. 15°27.64'E, 50°50.21'N. Platy outcrop of the porphyritic granite c. 0.3 km NW of the top of Czerwone Skałki Hill, in the left (eastern) bank of Czerwony Potok; vertical veinlet of gray quartz up to 3 cm thick with ore minerals in streaks with dimensions of c. 5×15 mm.

Outcrop 7. 15°26.85'E, 50°50.23'N. Small rock of porphyritic granite near a N-S path on the southern slope of Skalny Dom (Rock House) Hill c. 0.4 km of the top; Two nests of slightly

turbid gray quartz of dia. 10 and 17 cm with dispersed ore minerals.

Outcrop 8. 15°26.68'E, 50°50.34'N. A block of porphyritic granite c. 0.2 km SW of the top of Skalny Dom Hill; almost horizontal veinlet of gray quartz c. 1.3 cm thick and of visible length c. 40 cm contains dispersed ore minerals.

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* Dressler's Creek; Adolph Dreßler 1833–1881, painter of the Karkonosze Mts. landscapes (Rome-Dzida 2013, pp. 104–140).

Outcrop 9. 15°26.77'E, 50°50.46'N. Block of the porphyritic granite c. 0.1 km west of the Skalny Dom Hill top; lenticular nest (c. 20 cm) of gray quartz, microcline and albite with dispersed ore minerals.

Outcrop 10. 15°26.32'E, 50°50.25'N. Flat, almost horizontal outcrop of porphyritic granite c. 0.1 km west of Ciekoniek stream, c. 0.7 km north of the railway track; probably vertical veinlet of gray quartz with visible length c. 35 cm and thickness c. 1 cm with dispersed ore minerals.

INVESTIGATION METHODS

Preliminary separation of specimens for laboratory investigations was made during review under a stereoscope microscope. The preparations for the EPMA were glued on glass, polished and covered by carbon, silver or gold film depending on the elements to be determined. The quantitative analysis of chemical composition was made by the WDS electron probe micro-analytic method by use of the Cameca SX100 and ARL SEMQ analyzers. The applied analytical conditions were as follows: electron beam accelerating voltage 7–20 keV, beam current 8–20 nA, diameter of beam spot 3–10 µm, count time 4–25 sec. Some preparations, especially opened fluid inclusions (the method proposed by Dolomanova *et al.* 1966 and Eadington 1975, modified by A.K.), were frozen by liquid nitrogen or liquid helium during the analytical process. These X-ray peaks were used for quantitative analyses: Ag*Lα*, Al*Kα*, As*Lα*, Au*Lα*, Bi*Mα*, Br*Kα,* Ca*Kα*, Cd*Kα,* Cl*Kα,* Co*Kα,* Cu*Kα*, Fe*Kα*, Ge*Kα,* Hg*Mα*, F*Kα*, I*Kα,* In*Kα*, K*Kα*, Mg*Kα*, Mn*Kα*, Mo*Lα*, Na*Kα*, Nb*Lα*, Ni*Kα,* Pb*Mβ*, S*Kα*, Sb*Lα*, Se*Lα*, Sn*Kα,* Ta*Lα*, Te*Kα*, Ti*Kα*, Tl*Kα*, V*Kα*, W*Lα*, and Zn*Kα*. For carbon determination the parameters were as follows: voltage 10 keV, beam current 300 to 400 nA, the peak C*Kα* (Robaut *et al.* 2006). The following reference substances were applied: synthetic Ag_2S, $(Ag_{0.9}Au_{0.1})$, $Ag(Cl_{0.8}Br_{0.1}I_{0.1})$, Ag_2Te, Al, Bi_2S_3, CdS, Co, $CuInS_2$, GeSe, HgS, KCl, MgO, MnS, MoS_2, NaCl, Nb, Ni, Sb_2S_3, SnO_2, Ta, TiO_2, Tl_2S, ZnS and natural $CaAl_2Si_2O_6$, CaF_2, $CaWO_4$, $CuFeS_2$, FeAsS, PbS and $Pb_5(VO_4)_3Cl$. The element contents were calculated by the ZAF, Multi, CALCZAF, TRYZAF and CITZAF programs (Trincavelli and Castellano 1999; Armstrong *et al.* 2013; see also Llovet *et al.* 2021). Trace amounts of Sb were determined by the FAAS method (Sun and Li 2005; Bader 2011) with use of the AAS9000 spectrometer.

The XRD determinations were made by the X'Pert PRO MPD device with Cu*Kα* 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.

Fluid inclusions in the associated quartz were studied by the heating-freezing conventional method (Crawford 1981, pp. 75–100; 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 ±0.5°C and for Tm ±0.1°C. Fluid inclusions were also opened by indentation or in crushing stage and the chemical composition of the precipitate of the inclusion fluid was determined by EPMA. The same analytical method was used for inclusions opened by removal of the upper part of the host quartz in crushing stage with immediate freezing in liquid nitrogen or helium. Next the surface was close covered by the very fine gold foil with use of the micro-press instrument to obtain the preparation for electron microprobe analysis. The composition of the inclusion fluids was calculated on the basis of the freezing and electron probe analysis data. Fluid inclusions that could be applied to determine the fluid pressure have not been found, thus the Th values were used for description of the mineral crystallization conditions. Probably the pressure correction for the Th values would not exceed c. 60ºC (Kozłowski and Marcinowska 2007).

It was not possible to make sufficiently good quality optic photographs of eu- and subhedral crystals of the investigated "microminerals", thus very exact drawings were prepared by A.K. on the basis of the stereoscope microscope observations. Also the BSE images were recorded during EPMA by A.K. The investigations were made in the laboratories of University of Warsaw and University of Tūbingen.

RESULTS

Field work in the years 1970–1980 on the southern slope of the Wysoki Grzbiet (High Ridge, Izera Mts.) between Szklarska Poręba and Czech state border yielded samples in which 18 Sb minerals were identified in 10 outcrops of the Karkonosze granitoid at least 0.8 km distant from the contact of the batholith with its northern metamorphic envelope. Investigations of these samples revealed 1 native element (antimony), 1 alloy (Sb-bearing domeykite), 3 sulphides (getchellite, stibnite, willyamite), 10 sulphosalts (berthierite, boulangerite, bournonite, chalcostibite, falkmanite, famatinite, geocronite, robinsonite, semseyite, tetrahedrite-(Fe)), 1 oxide (cervantite), 1 oxysulphide (kermesite) and 1 antimonate (schafarzikite). In their parageneses or associations 16 ore minerals were found: 1 native element (bismuth), 10 sulphides (arsenopyrite, bismuthinite, bornite, chalcopyrite, chalcocite, galena, molybdenite, pyrrhotite, pyrite, sphalerite), 4 sulphosalts (aikinite, cosalite, emplectite, galenobismuthite) and 1 oxide (magnetite), see Table 1; representative chemical compositions are in Appendix 2 and crystallochemical formulae in Appendix 3. The Sb mineral specimens are very small ("microminerals") – from tenths of a millimetre to a few millimetres. They were identified by the methods of X-ray diffraction (Table 2) and EPMA (Tables 3–6).

Minerals	Outcrops, nos.									
	1	2	3	4	5	6	7	8	9	10
Native elements										
antimony	×			×						
bismuth		×		×						
Alloy										
Sb-bearing domeykite	×		×			×				
Sulphides										
getchellite	×						×			
stibnite	×	×	×		×	×	×		×	
willyamite			×							×
arsenopyrite			×							
bismuthinite			×	×	×	×		×		×
bornite	×	×			×					
chalcopyrite	×		×	×	×	×	×			×
chalcocite	×					×				
galena	×	×				×		×	×	×
molybdenite		×		×		×	×			
pyrrhotite		×			×			×	×	
pyrite	×	×	×	×	×	×	×	×	×	×
sphalerite						×				
Sulphosalts										
berthierite		×								
boulangerite	×				×			×	×	
bournonite	×	×		×		×		×		×
chalcostibite	×		×				×			×
falkmanite	×							×		
famatinite				×	×					×
geocronite		×		×						
robinsonite		×						×		
semseyite					×	×				
tetrahederite-(Fe)			×	×						
aikinite	×									×
cosalite					4				×	
emplectite	×									
galenobismutite						×				
Oxides										
cervantite							×			
magnetite					×					
Oxysulfide										
kermesite								×	×	
Antimonate										
schafarzikite							×			

Table 1. The found Sb minerals (in bold letters) and the associated other ore minerals from the investigated locations.

Antimony Sb*

This mineral has been used as a component of the antimony-bearing ore since very early antiquity and called *stimmi, stibi, Spiesglas* etc. (see above General ntroduction). A mineralogical approach to it may be found in Henckel's book (1725, pp. 80, 82 and 184); it is described separately as *regulus antimonii*. Distinctly as an individual mineral *nativ regulus antimonii* it is the subject of the Swab's paper (1748). Likewise Cronstedt (1760, pp. 213–215) included it as *gediegen Spiesglas antimonium natiuum ſeu* [or] *regulus antimonii natiuus* into his handbook. The antimony presence in ore parageneses of various deposits was also described, e.g. in Harz area (Schulze 1895, p. 2), in the State of Washington (Purdy Jr. 1951, p. 17), in the Finnish deposit Seinäjoki (Pääkkönen 1966) or in the Swedish mine Getberg in Långban area (Zakrzewski 1984); up to now it has been found in c. 400 locations across the entire Earth's surface (here and below these numbers were estimated on the basis of the Mindat informations). For 3 occurrences in Lower Silesia known before 2024 see Appendix 1.

In the considered area antimony has been found in two outcrops. In outcrop 1 antimony formed rhombohedral sub- and euhedral crystals (hexagonal scalenohedral class $\bar{3}\ m$) in size up to 0.4 mm that crystallized on subhedral stibnite grains and this one – on subhedral pyrite (Text-fig. 3A). Thus the sequence of crystallization is clear, from the pyrite (oldest) to antimony (youngest), moreover the sub- and euhedral habits indicate slow and quiet crystallization, probably with changing composition of the parent fluids of the minerals – from Fe and S rich with next decrease of Fe and incoming Sb and later (almost) lack of S. The main admixture elements in antimony are Pb (c. 1–1.5 wt.%) and As (c. 0.6–1.1 wt. %) and one (earliest of the analysed crystals) contained almost 0.9 wt. % Bi (Table 3) Distinctly lower are admixtures

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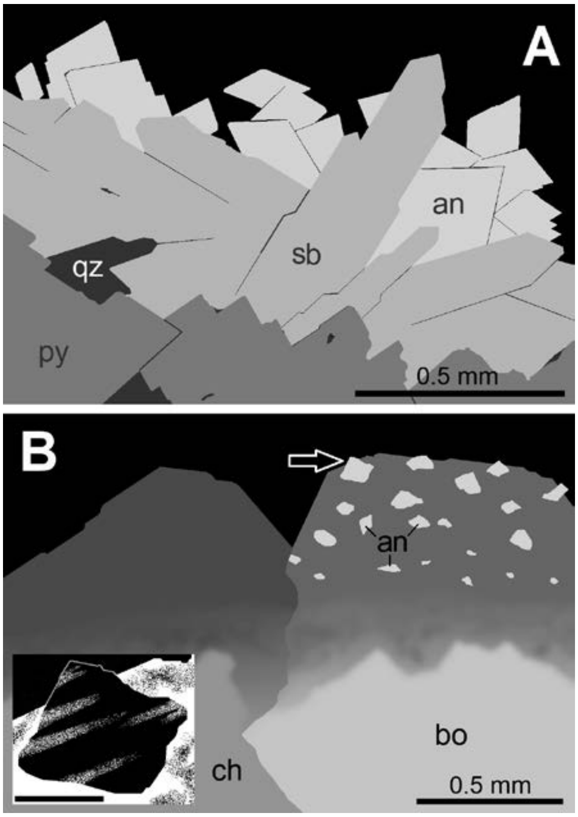
* Mineral formulae in the paragraph titles are theoretical; for the formulae of the investigated Sb mineral specimens see Tables 3–6.



Text-fig. 3. A – Antimony (an), subhedral crystals on stibnite (sb), py – pyrite, qz – quartz; outcrop 1. B – Small crystals of antimony (an) in altered bournonite (bo) near chalcopyrite (ch), external dark-gray zones of the two latter are altered into a mixture of fine grains of several minerals; outcrop 4. BSE images. The insert presents the antimony grain marked in the part B by arrow, S*Kα* radiation image, the upper part of the grain is separated from the background by added line; scale bar 0.05 mm. Note: here and below the used abbreviations of the mineral names are shortened to minimize their influence on the image.

of Cu (c. 0.5 wt. %) and Fe (from undetectable to c. 0.4 wt. %). The admixture elements were of too low concentrations to form their own minerals when antimony crystallized (it contained c. 0.95–0.98 Sb apfu, see Table 3). In outcrop 4 antimony occurs in quite a different association (Text-fig. 3B). The paragenesis: chalcopyrite and bournonite was chemically altered in the outer zones to a mixture of (probably) sulphides with a high content of iron sulphide maybe partly amorphous. During decomposition of bournonite Sb crystallized in the altered zone in native form as subhedral grains up to 0.1 mm in size. These crystals contain streaks of S, which are not in agreement with their growth zones; most probably sulphur diffused inside the crystals (see insert in Text-fig. 3). Hence, probably when antimony crystallized, the activity of S was low and later, after it increased, it could migrate into the crystals, like it was found for elements in other minerals (cf. Beutell 1913, 1916, pp. 270–472; Liu and Beaudoin 2021; Kozłowski and Matyszczak 2023, text-fig. 5 and pp. 238–239). Admixture elements contents are low in these antimony crystals (Fe c. 0.3–0.4 wt. %, Cu c. 0.4–0.8 wt. %, see Table 3). The altered zone of chalcopyrite and bournonite contained also quartz crystals with trapped inclusions of the host mixture of minerals and few fluid inclusions. This made it possible to determine the conditions of antimony crystallization.

Domeykite $Cu_3(As,Sb)$

Varieties of domeykite were exploited with Cu ores already in Antiquity, e.g. in the Sinai peninsula in Chalcocite and Early Bronze ages (Ilani and Rosenfeld 1994) or in mines in the Toroud area, Iran, at least in the 2nd millennium BC (Emami 2014), though not always is there evidence that this ore component was a Sb-bearing type. However, copper alloy artifacts found in the Tepe Yahya excavations and which have been produced since c. 5500 BC most probably from the ores (with Sb-bearing domeykite) of the Iranian deposits at the Anarak-Talmessi-Meskani region, contain ≤3 wt. % Sb and ≤7 wt. % As (Thornton *et al.* 2002). Some Japanese old copper products from Heian age (8–12 century AD), mostly coins, were probably made from an alloy with Sb-rich domeykite as its component (Kitakaze and Aoshima 2019).

The Cu_3As mineral was first described by Domeyko (1845, pp. 138–139) as *cobre blanco* i.e. white copper, occurring in sulphide ores at Calabazo Mt. in Illapel department, as well as in mines in San Antonio, Copiapó, Chile. The name domeykite for "white copper" was given by Haidinger (1845, p. 562). Later Domeyko (1960, pp. 131–133) listed domeykite and condurrite*

as synonyms of cobre blanco; he added the Algodones mine in Coquimbo and Cerro de las Yeguas in Rancagua to the Chilean occurrences. Even more Chilean occurrences of domeykite was added in his next book of mineralogy (Domeyko 1879, pp. 242–245) and those in other countries completed the list. Now c. 80 locations with domeykite are known in all countries, but it is not sure in what part of them this mineral is the Sb-bearing variety.

Koenig (1900) described domeykite with Sb ad-

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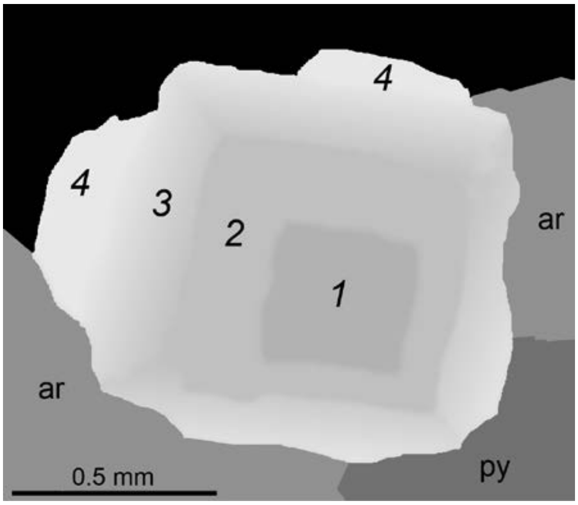
* Condurrite (see Blyth 1849, Field 1857, Bristow 1861, p. 92) is not a mineral but mixture of domeykite etc. (Embrey 1958).

Mineral, location		d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
Antimony	Outcrop 1	3.899	29	3.198	100	2.282	55	2.178	35	1.898	24	1.785	21	1.421	15
	Jahazpur (1)	3.891	27	3.199	100	2.286	58	2.180	33	1.901	20	1.793	25	1.417	10
Berthierite	Outcrop 2	4.362	43	3.675	61	3.637	76	3.394	72	3.182	49	3.008	100	2.873	39
	Toyoha mine (2)	4.37	50	3.67	70	3.64	80	3.39	80	3.19	50	3.01	100	2.87	50
Boulangerite	Outcrop 5	3.726	100	3.435	18	3.291	16	3.225	52	3.037	44	2.827	38	2.688	31
	Janggun mine (3)	3.75	100	3.44	20	3.32	20	3.22	50	3.03	40	2.823	50	2.692	30
Bournonite	Outcrop 1	3.355	76	2.852	100	2.364	56	1.819	61	1.669	66	1.439	29	1.230	36
	Kosaka mine (4)	3.36	75	2.85	100	2.37	50	1.825	50	1.676	75	1.446	25	1.235	25
Cervantite	Outcrop 7	3.445	38	3.069	100	2.939	41	2.647	33	1.869	40	1.768	19	1.715	26
	Clara mine (5)	3.440	31	3.065	100	2.945	47	2.643	29	1.862	33	1.775	24	1.719	18
Chalcostibite	Outcrop 7	3.078	100	2.996	87	2.311	62	2.119	35	2.896	41	1.832	88	1.768	75
	Dúbrava mine (6)	3.09	100	3.01	100	2.31	50	2.12	40	1.900	40	1.825	80	1.759	80
Sb-bearing domeykite	Outcrop 6	3.949	43	3.055	33	2.147	52	2.062	100	1.968	44	1.892	74	1.309	53
	Romehra (7)	3.947	40	3.054	40	2.149	40	2.060	100	1.967	50	1.890	70	1.307	50
Falkmanite	Outcrop 8	4.006	24	3.743	100	3.217	19	3.015	54	2.809	70	2.044	33	1.852	54
	Pinnacles mine (8)	4.01	20	3.74	100	3.22	30	3.02	50	2.82	80	2.04	40	1.86	50
Famatinite	Outcrop 10	3.068	100	2.657	59	1.980	34	1.893	76	1.610	66	1.339	54	1.232	63
	Synthetic (9)	3.071	100	2.664	50	1.985	40	1.895	80	1.614	70	1.342	50	1.232	60
Geocronite	Outcrop 2	4.457	41	3.821	34	3.720	58	3.536	100	3.398	78	3.066	85	2.976	60
	Silver King mine(10)	4.46	40	3.83	40	3.71	60	3.54	100	3.39	80	3.06	90	2.98	70
Getchellite	Outcrop 7	4.966	54	4.576	43	4.448	84	3.624	72	2.894	100	2.773	58	2.544	63
	Getchell mine (11)	4.97	50	4.60	50	4.44	80	3.63	70	2.89	100	2.80	50	2.54	60
Kermesite	Outcrop 8	3.292	57	2.908	70	2.676	100	2.485	59	2.247	36	2.036	52	1,780	65
	Globe mine (12)	3.30	50	2.90	60	2.68	100	2.48	50	2.25	40	2.03	50	1.784	70
Robinsonite	Outcrop 8	4.042	68	3.911	83	3.785	54	3.664	63	3.394	100	3.175	72	3.033	71
	Red Bird mine (13)	4.04	80	3.92	80	3.79	60	3.66	60	3.39	100	3.18	60	3.03	80
Schafarzikite	Outcrop 7	3.234	55	3.049	67	1.681	100	1.314	73	1.166	52	1.042	31	1.009	15
	Synthetic (14)	3.232	50	3.047	50	1.676	100	1.309	60	1.158	60	1.050	25	1.015	20
Semseyite	Outcrop 5	3.822	24	3.410	35	3.368	57	3.259	64	2.968	100	2.847	36	2.695	37
	Bohutín (15)	3.820	30	3.414	30	3.370	51	3.257	67	2.966	100	2.858	34	2.699	34
Stibnite	Outcrop 7	5.068	41	3.492	100	2.758	27	2.526	47	2.103	37	1.928	53	1.720	21
	Ichinokawa (16)	5.07	40	3.50	100	2.76	30	2.52	40	2.10	30	1.933	50	1.728	30
Tetrahedrite	Outcrop 4	3.681	100	2.990	91	2.611	26	2.459	17	1.833	61	1.568	37	1.047	14
	Wolfsgruben (17)	3.685	100	2.988	96	2.607	23	2.462	14	1.829	64	1.565	35	1.052	17
Willyamite	Outcrop 9	2.620	100	2.382	69	1.763	51	1.625	33	1.553	45	1.270	38	1.073	35
	Consols mine (18)	2.618	100	2.386	73	1.763	56	1.629	37	1.560	48	1.274	46	1.080	31

Table 2. Representative X-ray powder diffraction patterns of the antimony minerals from the southern slope of Izera Mts., Karkonosze pluton, for outcrop locations see Text-fig. 2. The selection of the most intense reflections of the samples is shown; intensity values are recalculated to the 100-grade scale if necessary. Numbers in the parentheses pertain to the following references: (1) Ranawat *et al.* 2005, (2) Ohta 1979, (3) Lee and Imai 1993, (4) Yamaoka *et al.* 1983, (5) authors' data 2001, specimen from the mine in Oberwolfach, Freiburg region, Baden-Württemberg, Germany, (6) Hak *et al.* 2020, (7) Singh *et al.* 2002, (8) McQueen 1987, (9) Gaines 1957, (10) Douglas *et al.* 1954, (11) Weissberg 1965, (12) Berry and Thompson 1962, (13) Berry *et al.* 1952, (14) Leverett *et al.* 2012, completed by the authors' data, (15) Litochleb *et al.* 2008, (16) Berry and Thompson 1962, (17) authors' data 2004, specimen from the mine in Seiz, Liesingtal, Leoben district, Austria, (18) authors' data 2009, specimen from the mine in Broken Hill, Yancowinna Co., NSW, Australia.

mixture (0.78 wt. %) and gave this mineral a new name *stibio-domeykite*, however, recently evaluated as obsolete (Robinson 2004). Koenig (1903) also synthesized Sb-bearing domeykite (*stibiodomeykite*) which contained 1.26 wt. % Sb.

Domeykite till now apparently was not identified in Poland. The Sb-bearing domeykite in the investigated area was found in outcrops 1, 3 and 6. It forms isometric crystals (hextetrahedral class $\overline{4}\,3m$) usually as poorly subhedral grains probably alluding to the cubic habit (Text-fig. 4). Two grains from outcrop 1 had size 0.4 and 0.6 mm; they contained c. 0.4–0.5 wt. % Sb, moreover Fe and Ni admixtures and one Co as well (Table 3). The chemical composition was almost uniform in each grain from outcrop 1. Similarly minor changes of composition have individual grains (size 0.7 and 0.8 mm) from outcrop 6: in wt. % respectively Sb c. 1.7–1.8 and c. 0.5, Pb c.



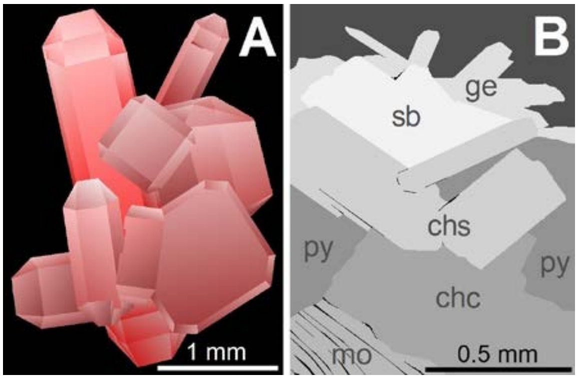
Text-fig. 4. Sb-bearing domeykite, grain with zones 1–4 of various Sb contents, ar – arsenopyrite, py – pyrite; outcrop 3. BSE image.

1.2–1.4 and c. 0.5, Fe c. 0.2 in both, S 0.02–0.04 and 0.05–0.06; only Zn content was 0.07–0.10 in the first grain but below detection limit in the second one. Thus the chemical data would suggest rather stable conditions of formation of individual grains. A different scheme of chemical composition was found in the grain with size of 1.3 mm from outcrop 3. It has distinct four zones with rectangular borders, visible in the BSE image (Text-fig 4) and connected with changes of the admixture contents. The inner zone *1* contains Sb (in wt. %) c. 0.3, zone *2* – c. 0.8, zone *3* – c. 1.4 and the outer zone *4* – 1.8 and only this one c. 0.16 Bi. Thus conditions of growth of this grain varied and the changes were rapid after periods of quiet growth, because the zone borders are almost sharp and each zone itself is homogeneous. Domeykite from all outcrops was in association with Sb minerals (Table 1) and always contained Sb; no Sb-free specimens were found.

Getchellite $SbAsS_3$

The mineral called later getchellite was found 1962 in the Getchell mine at Adam Peak in Osgood Mts., Nevada (Weissberg 1965). It was associated with orpiment, realgar, cinnabar and stibnite in this epithermal occurrence. The same year the finding of getchellite was described from Zarshuran in Iran (Bariand *et al.* 1965). Stability of getchellite at 100 and 200ºC was evidenced by the phase equilibria calculations published by Sobott (1995). However, in the Zarshuran gold mineralization in NW Iran its formation temperature was evaluated as 260–300ºC (Asadi *et al.* 2000), thus much higher than for the epithermal crystallization. But Mehrabi *et al.* (2003) published fluid inclusion Th ranges 124–244, 128–236, 129–142, 129–197 and 149–162 ºC for various mineralization episodes in this deposit, and Yousefi *et al.* (2019) the fluid inclusion Th values for the getchellite-bearing ores presented approximately as c. 260ºC. The solid solutions As_2S_3-Sb_2S_3, getchellite inclusively, were discussed on the basis of the minerals of this deposit (Mehrabi 2008). The known occurrences of getchellite are not numerous (c. 20 in all countries but not in Poland); it is known e.g. from Japanese mine Toya-Takarada (Yunungsih 2016), Chauvai and Khaidarkan deposits in Kyrgyzstan (Kolesar *et al.* 1991) or Jas Roux in France (Bourgoin *et al.* 2011).

In the studied area getchellite was recognized in two outcrops: 1 and 7. In the first one it forms a 4 mm long group of euhedral light (poppy) red, turbid crystals of size 0.5 to 3 mm (Text-fig. 5A). The crystals are monoclinic and have lath or platy habits, which may be easily related to the prismatic class *2/m*. The getchellite mineral association includes here 7 other Sb minerals: antimony, Sb-bearing domeykite, stibnite, boulangerite, bournonite, chalcostibite and falkmanite, and 7 ore minerals without Sb as the main component (Table 1), though the group of the getchellite crystals formed on and partly in quartz, separately from other ore minerals. In chemical composition of this getchellite sample the admixture of Pb has the highest concentrations (c.0.6 wt. %), next Cu (c. 0.2–0.3 wt. %), Se (0.1–0.2 wt. %) and Bi (c. 0.1 wt. %); Te, Ag and P presence is lower:



Text-fig. 5. A* – Getchellite, a group of crystals; outcrop 1. B – Getchellite (ge) on stibnite (sb) and chalcostibite (chs), associated with pyrite (py), chalcocite (chc) and molybdenite (mo); outcrop 7. BSE image.

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* In the text figure chapters the asterisk indicates that the mineral picture was drawn by AK.

Mineral and location	No.	Sb	As	Bi	Pb	Fe	Co	Ni	Cu	Zn	S	Σ, wt. %
Antimony												
Outcrop 1	01	97.862	0.649		1.008				0.466			99.985
	02	96.829	0.769		1,492	0.365			0.531			99.986
	03	96.106	1.128	0.882	1.028	0.260			0.530			99,934
Outcrop 4	04	99.151	trace			0.416			0.421		trace	99.988
	05	98.820	trace			0.325			0.845		trace	99.990
Sb-bearing domeykite												
Outcrop 1	06	0.366	27.959			0.399		0.243	71.005			99.972
	07	0.502	27.814			0.479	0.132	0.307	70.756			99.990
Outcrop 3 (in one grain*)	08	0.321	27,995			0.336		0.199	71.120			99.971
	09	0.823	27.643			0.338		0.044	71.134			99.973
	10	1.414	27.202			0.314			71.056			99.986
	11	1.820	26.814	0.155		0.125			71.084			99.998
Outcrop 6 (in one grain)	12	1.720	26.706		1.232	0.187			70.014	0.097	0.036	99.992
	13	1.850	26.571		1.382	0.166			69.901	0.073	0.024	99.967
Outcrop 6 (in one grain)	14	0.502	27.681		0.544	0.230			70.963		0.047	99.967
	15	0.457	27.686		0.464	0.185			71.131		0.060	99.983

* analyses in zones of the Sb-bearing domeykite grain, vide Text-fig. 4: 08 – zone 1 (central), 09 – zone 2, 10 – zone 3, 11 – zone 4 (outside). Crystallochemical formulae (apfu) calculated for the total of all elements as one atom (nos. 01–05) and for the total (As+Sb+S) as one atom (nos. 06–15).

01: $Sb_{0.975}As_{0.010}Cu_{0.009}Pb_{0.006}$
02: $Sb_{0.961}As_{0.012}Cu_{0.010}Pb_{0.009}Fe_{0.008}$
03: $Sb_{0.954}As_{0.018}Cu_{0.011}Pb_{0.006}Fe_{0.006}Bi_{0.005}$
04: $Sb_{0.983}Fe_{0.009}Cu_{0.008}$
05: $Sb_{0.977}Cu_{0.016}Fe_{0.007}$
06: $(Cu_{2.970}Fe_{0.019}Ni_{0.011})_{\Sigma 3.000}(As_{0.992}Sb_{0.008})_{\Sigma 1.000}$
07: $(Cu_{2.966}Fe_{0.023}Ni_{0.014}Co_{0.006})_{\Sigma 2.999}(As_{989}Sb_{0.011})_{\Sigma 1.000}$
08: $(Cu_{2.974}Fe_{0.016}Ni_{0.009})_{\Sigma 2.999}(As_{0.993}Sb_{0.007})_{\Sigma 1.000}$
09: $(Cu_{2.980}Fe_{0.016}Ni_{0.002})_{\Sigma 2.998}(As_{0.982}Sb_{0.018})_{\Sigma 1.000}$
10: $(Cu_{2.984}Fe_{0.015})_{\Sigma 2.999}(As_{0.969}Sb_{0.031})_{\Sigma 1.000}$
11: $(Cu_{2.994}Fe_{0.006})_{\Sigma 3.000}(As_{0.958}Sb_{0.040}Bi_{0.002})_{\Sigma 1.000}$
12: $(Cu_{2.964}Pb_{0.016}Fe_{0.009}Zn_{0.004})_{\Sigma 2.993}(As_{0.959}Sb_{0.038}S_{0.003})_{\Sigma 1.000}$
13: $(Cu_{2.968}Pb_{0.018}Fe_{0.008}Zn_{0.003})_{\Sigma 2.997}(As_{0.957}Sb_{0.041}S_{0.002})_{\Sigma 1.000}$
14: $(Cu_{2.977}Fe_{0.011}Pb_{0.007})_{\Sigma 2.995}(As_{0.985}Sb_{0.011}S_{0.004})_{\Sigma 1.000}$
15: $(Cu_{2.984}Fe_{0.009}Pb_{0.006})_{\Sigma 2.995}(As_{0.985}Sb_{0.010}S_{0.005})_{\Sigma 1.000}$

Table 3. Chemical composition of antimony and native alloy Sb-bearing domeykite, representative analyses; empty cells – component below detection limit (<~0.001 wt. %); if no mention, one analysis is for one specimen.

<0.02–0.04, c. 0.03 and 0.01–0.02 wt. %, respectively (Table 4).

Although getchellite rarely forms euhedral habits, another studied specimen from the Karkonosze granitoid (outcrop 7) consists of euhedral and subhedral crystals (Text-fig 5B). Its colour is also red but with light violet tint, the crystals are to c. 0.5 cm long laths. It crystallized on stibnite and chalcostibite in association with pyrite, chalcocite and molybdenite, in and partly on quartz. In the same outcrop cervantite was found (Table 1). Admixture elements in chemical composition of getchellite from this outcrop varied distinctly in one grain (in wt. %, higher values in early part of the crystal): Pb <0.1–0.4, Cu <0.1–0.4, Fe 0.07–0.09, Se 0.03–0.04, Mo ≤0.001–0.03.

Stibnite Sb_2S_3

Stibnite has been used as the component of Sb ores since prehistoric periods and its present name was moulded from an ancient word *šimzida* or *šimbizi* later changed to *stimmi* and *stibi* (see above General introduction). Agricola (1561) used the name *Spisglas* or *Spiesglass*, The 16th/17th century information on stibnite as *Spießglas* (Spieß – spear, an allusion to the stibnite crystal habit) and other Sb-bearing substances, not exactly distinguished from this mineral, was presented mostly in the alchemical context. Such an opinion was supported by Roger Bacon's (English scientist and philosopher 1214–1292) studies and knowledge, and it was prepared under the name "Basilius Valentinus" (1604, pp. 236–296),

Mineral and location	No.	As	Sb	Bi	Fe	Co	Ni	Zn	Cu	Ag	Pb	S	Se	Te	Σ, wt. %
Getchellite															
Outcrop 1	01	23.122	43.419	0.077		0.021*			0.297	0.029	0.573	32.211	0.204	0.036	99.989
	02	22.793	43.774	0.131		0.008*			0.192	0.025	0.640	32.241	0.141	0,021	99.995
Outcrop 7 (in one grain)	03	22.413	44,241		0.087	0.026■			0.448		0.417	32.319	0.044		99.995
	04	20.951	46.895		0.073				0.041		0.062	31.949	0.026		99.997
Stibnite															
Outcrop 1	05	0.573	69.897	0.617					0.319	0.092		28.354	0.101	0.031	99.985
	06	0.642	69.768	0.494					0.453	0.063		28.394	0.140	0.037	99.991
Outcrop 2	07	0.379	70.599	0.246					0.243	0.035		28.244	0.162	0.070	99.975
	08	0.421	70.533	0.308					0.211	0.032		28.314	0.142	0.027	99.988
Outcrop 3	09	0.464	69.730	0.678					0.487	0.063		28.306	0.185	0.075	99.989
Outcrop 5	10	0.377	70.278	0.619					0.299			28.348	0.046	0.019	99.986
	11	0.330	70.218	0.676					0.262			28.279	0.069	0.040	99.874
Outcrop 6	12	0.310	70.701	0.062				0.039	0.376			28.430	0.070		99.988
	13	0.288	70.737	0.124				0.019	0.338			28.383	0.094		99.983
Outcrop 7	14	0.537	70.052	0.121		0.015	0.056		0.592			28.511	0.078	0.027	99.989
	15	0.605	69.738	0.186		0.037	0.052		0.718			28.565	0.049	0.032	99.982
Outcrop 9	16	0.244	70.708	0.065		0.036	0.019		0.357	0.034		28.389	0.070	0.068	99.990
Willyamite															
Outcrop 3	17	0.103	57.229		0.025	24.491	3.026	0.030				15.014	0.074		99.992
	18	2.216	54.362		0.027	25.186	2.884					15.282	0.038		99.995
Outcrop 10	19	0.211	56.754	0.196	0.081	26.362	1.159				0.097	15.008	0.113		99.981
	20	0.180	56.887	0.095	0.104	26.449	1.073				0.094	15.043	0.070		99.995

Crystallochemical formulae (apfu) calculated for the total of all components as five atoms (nos. 01–04), or for (S+Sb+Te) atom amounts in the theoretical formulae (nos. 05–20).

01: $\mathrm{As_{0.912}P_{0.002}Sb_{1.062}Bi_{0,001}Pb_{0.008}Cu_{0.014}Ag_{0.001}S_{2.991}Se_{0.008}Te_{0.001}}$
02: $\mathrm{As_{0.906}P_{0.001}Sb_{1.071}Bi_{0,002}Pb_{0.009}Cu_{0.010}Ag_{0.001}S_{2.994}Se_{0.005}Te_{0.001}}$
03: $\mathrm{As_{0.889}Sb_{1.080}Pb_{0.006}Cu_{0.021}Fe_{0.005}Mo_{0.001}S_{2.996}Se_{0.002}}$
04: $\mathrm{As_{0.841}Sb_{1.158}Pb_{0.001}Cu_{0.002}Fe_{0.002}S_{2.995}Se_{0.001}}$
05: $\mathrm{(Sb_{1.944}As_{0.026}Bi_{0.010}Cu_{0.017}Ag_{0.003})_{\Sigma 2.000}(S_{2.994}Se_{0.005}Te_{0.001})_{\Sigma 3.000}}$
06: $\mathrm{(Sb_{1.936}As_{0.029}Bi_{0.008}Cu_{0.024}Ag_{0.002})_{\Sigma 1.999}(S_{2.993}Se_{0.006}Te_{0.001})_{\Sigma 3.000}}$
07: $\mathrm{(Sb_{1.965}As_{0.016}Bi_{0.004}Cu_{0.012}Ag_{0.001})_{\Sigma 1.998}(S_{2.991}Se_{0.007}Te_{0.002})_{\Sigma 3.000}}$
08: $\mathrm{(Sb_{1.963}As_{0.019}Bi_{0.005}Cu_{0.011}Ag_{0.001})_{\Sigma 1.999}(S_{2.993}Se_{0.006}Te_{0.001})_{\Sigma 3.000}}$
09: $\mathrm{(Sb_{1.939}As_{0.021}Bi_{0.011}Cu_{0.025}Ag_{0.002})_{\Sigma 1.998}(S_{2.990}Se_{0.008}Te_{0.002})_{\Sigma 3.000}}$
10: $\mathrm{(Sb_{1.957}As_{0.017}Bi_{0.010}Cu_{0.016})_{\Sigma 2.000}(S_{2.997}Se_{0.002}Te_{0.001})_{\Sigma 3.000}}$
11: $\mathrm{(Sb_{1.959}As_{0.015}Bi_{0.011}Cu_{0.014})_{\Sigma 1.999}(S_{2.996}Se_{0.003}Te_{0.001})_{\Sigma 3.000}}$
12: $\mathrm{(Sb_{1.962}As_{0.014}Bi_{0.001}Cu_{0.019}Zn_{0.002})_{\Sigma 1.998}(S_{2.997}Se_{0.003})_{\Sigma 3.000}}$
13: $\mathrm{(Sb_{1.965}As_{0.012}Bi_{0.002}Cu_{0.018}Zn_{0.001})_{\Sigma 1.998}(S_{2.996}Se_{0.004})_{\Sigma 3.000}}$
14: $\mathrm{(Sb_{1.938}As_{0.023}Bi_{0.002}Cu_{0.030}Ni_{0.003}Co_{0.001})_{\Sigma 1.997}(S_{2.996}Se_{0.003}Te_{0.001})_{\Sigma 3.000}}$
15: $\mathrm{(Sb_{1.927}As_{0.027}Bi_{0.003}Cu_{0.038}Ni_{0.002}Co_{0.003})_{\Sigma 2.000}(S_{2.997}Se_{0.002}Te_{0.001})_{\Sigma 3.000}}$
16: $\mathrm{(Sb_{1.964}As_{0.011}Bi_{0.001}Cu_{0.019}Ag_{0.001}Ni_{0.001}Co_{0.002})_{\Sigma 1.999}(S_{2.995}Se_{0.003}Te_{0.002})_{\Sigma 3.000}}$
17: $\mathrm{(Co_{0.886}Ni_{0.110}Fe_{0.001}Zn_{0.001}As_{0.003}Sb_{1.002})_{\Sigma 2.003}(S_{0.998}Se_{0.002})_{\Sigma 1.000}}$
18: $\mathrm{(Co_{0.896}Ni_{0.103}Fe_{0.001}As_{0.062}Sb_{0.936})_{\Sigma 1.998}(S_{0.999}Se_{0.001})_{\Sigma 1.000}}$
19: $\mathrm{(Co_{0.953}Ni_{0.042}Fe_{0.003}Pb_{0.001}As_{0.006}Sb_{0.993}Bi_{0.002})_{\Sigma 2.000}(S_{0.997}Se_{0.003})_{\Sigma 1.000}}$
20: $\mathrm{(Co_{0.955}Ni_{0.039}Fe_{0.004}Pb_{0.001}As_{0.005}Sb_{0.994}Bi_{0.001})_{\Sigma 1.999}(S_{0.998}Se_{0.002})_{\Sigma 1.000}}$

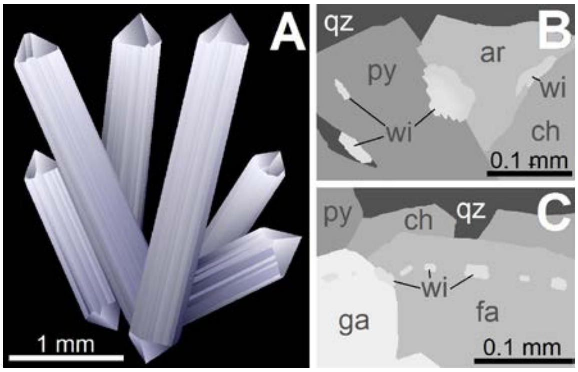
Table 4. Chemical composition of Sb sulphides, representative analyses; empty cells – component below detection limit (<~0.001 wt. %); if no mention, one analysis is for one specimen. * P, ■ Mo.

in fact by Johann Thölden. Spießglas as a synonym of stibnite survived almost to contemporary time. Early modern description of stibnite with use of this name (in French *stibine*) was given by Beudant (1832, pp. 421–424), who cited as well its synonym names *Antimonglanz* and *Grauspiesglanzerz*.

Apart from the metallurgical, ceramic, medical or cosmetic use stibnite was (and is) a valued collectible specimen. Probably the best known source of the unusually large euhedral orthorhombic (*mmm* class) crystals of stibnite of length more than 50 cm and reportedly longer than 1 m was in the Japanese Ichinokawa mine in Ehime prefecture (Rickwood 1981, Bancroft 1988, Ito 2016, Minakawa 2018). Stibnite is apparently the most commonly occurring Sb mineral (c. 3800 locations in the whole world). Szakáll *et al.* (2000) described 22 of its occurrences in Hungary, Chovan *et al.* (2002a) – its extensive presence in Sb ores of W. Carpathians and E. Alps, etc.

In the 65 Lower Silesian locations of Sb minerals recognized hitherto stibnite was found in 24 ones (see Appendix 1). Moreover, among 10 outcrops with Sb minerals investigated in this research stibnite was identified in 7 of them (Table 1). A group of almost perfectly euhedral orthorhombic crystals (dipyramidal class *mmm*) with a length of 1.8 to 3.2 mm occurred in outcrop 3 (Text-fig. 6A). They have striations along the *C* axis on the prism faces, other faces are smooth. Two of the crystals were in one of their ends overgrown by quartz. The colour of the crystals was pale gray with a light bluish coating. Crystals in other places are subhedral, e.g. in outcrop 1 (Text-fig. 3) or outcrop 7 (Text-fig. 5). Also stibnite crystals from other outcrops (2, 5, 6 and 9) are subhedral and their size is ≤1 mm; they form groups (grains) of up to 10–12 crystals. Stibnite associates in the studied area with the following Sb minerals: antimony, domeykite, getchellite, berthierite, boulangerite, bournonite, chalcostibite, falkmanite, famatinite, geocronite, robinsonite, semseyite, tetrahedrite-(Fe), cervantite, schafarzikite and kermesite. For the ore minerals not containing Sb as their main component but co-occurring with stibnite see Table 1.

The analysed grains of stibnite differ in their contents of the admixture elements, especially the specimens from different outcrops; in the same outcrop differences are small. Generally, stibnite contains (in wt. %) c. 0.24–0.64 As, 0.06–0.68 Bi, <0.001–0.04 Co, <0.001–0.06 Ni, <0.001–0.04 Zn, 0.21–0.72 Cu, <0.001–0.09 Ag, 0.05–0.18 Se and <0.001–0.08 Te; Fe and Pb were below the detection limit (<0.001) in all the analysed grains (Table 4). However, the scattering of the contents in specimens from the same outcrop was much smaller, e.g. As in outcrop 1 ranged from 0.57 to 0.64 wt. % and in outcrop 6 from 0.29 to 0.31 wt. %. The differences for Bi were for outcrop 5 from 0.62 to 0.68 wt % but for outcrop 7 from 0.12 to 0.19 wt. % (Table 4). Also each analysed grain was chemically almost homogeneous, without distinct variations of composition in its volume. This suggests relatively small changes of crystallization conditions in one outcrop but quite significant differences between various outcrops. Alterations of stibnite were not observed except for one of the grains from outcrop 9, which was largely transformed probably by weathering or epithermal conditions into kermesite. Other grains in all the checked outcrops were in quartz, either as solid inclusions or sometimes in small closed voids, thus completely isolated from weathering factors. Small needle stibnite inclusions in quartz host were also found e.g. in Ukrainian Carpathians (Galiy *et al.* 1990, phot. 10).



Text-fig. 6. A* – Stibnite, a group of crystals; outcrop 3. B – Willyamite (wi), zonal and homogeneous grains inside arsenopyrite (ar), chalcopyrite (ch) and pyrite (py); outcrop 3. BSE image. C – Willyamite grains in famatinite (fa) and galena (ga), ch – chalcopyrite, py – pyrite; outcrop 10. BSE image.

Willyamite CoSbS

This Co-Sb sulphide was found for the first time in Consols mine at Broken Hill, Yancowinna Co., NSW, Australia; it was called from the aboriginal name of Broken Hill which is Willyama (Pittman 1893). Chemically it was determined as *sulph-antimonide of nickel and cobalt* and its connection with ullmannite (NiSbS) was indicated (op. cit). Willyamite as an individual mineral became the commonly listed component of the Broken Hill ore (see e.g. Stillwell 1926a). However, Palache *et al.* (1944, pp. 301–392) included it in ullmannite as cobaltian variety, but on the basis of re-examination of the specimens from the type locality Cabri *et al.* (1970) redefined it as a mineral which is the portion of the (Co,Ni)SbS series with cobalt in excess of nickel; they also presented distinct zoning of its chemical composition. It forms pseudocubic crystals but its structure is evaluated as monoclinic or triclinic.

Willyamite occurs infrequently (c. 30 locations known in all countries) as very subordinate component of Ni-Co-As-Sb-Fe-Pb-S ores, sometimes as relatively large grains, but also as fine inclusions e.g. in galena. Its representative occurrences were described e.g. from the Espeland galena mine near Vegårshei, Aust-Agder county, S Norway (Naik *et al.* 1976), Pb-Zn-Ag-(Co-Ni-Sb) sulphidic ore from Hultebo mine, Tunaberg area, central Sweden (Dobbe 1991), Pb-Zn-Ag-Sb deposit of Argentiera, Nurra region in NW Sardinia* (Veneradi Pirri 1992), vein-type Mari Rosa and Juncalón Sb deposits in Central-West Spain (Ortega and Vindel 1995), in sulphide Cu-Zn-Co-Ni ore of Outokumpu mine in E Finland (Weiser *et al.* 2008) or in sulphide Cu-Co polymetal ore from Beiyi mine, Shilu district, Hainan, China (Mikulski *et al.* 2012).

So far willyamite probably has been found at two places in Poland. At Karniowice near Cracow in a hydrothermally altered zone of travertine "within euhedral crystals of galena [there occurred a] single grain of mineral representing gersdorffite-ullmannite-willyamite series(?)" (Czerny 1992, p. 10). Also the presence of willyamite in Lower Silesia, Poland, was mentioned by Piestrzela (2019) from the formerly exploited Sn-Co Krobica-Gierczyn deposits in the Stara Kamienica schist belt in the N envelope of the Karkonosze pluton, but the sampling location is not precise.

In the part of the Karkonosze pluton currently researched by the authors willyamite was found in outcrops 3 and 10. In the first one subhedral to anhedral grains of this mineral ≤0.08 mm in size occurred in pyrite, on pyrite in quartz and between pyrite and arsenopyrite or chalcopyrite and arsenopyrite crystals (Text-fig. 6B). In outcrop 10 willyamite inclusions (size 0.01–0.02 mm) were found along the growth zones of famatinite and galena and between crystals of these minerals (Text-fig. 6C). The positions of the willyamite grains in the samples of both outcrops indicate paragenetic relations with the neighbouring minerals. Chemical analyses demonstrate that the studied specimens are close to the CoSbS end of the willyamite–ullmannite series (Co 0.886–0.955 apfu, Ni 0.039–0.110 apfu, Table 4, items 17–20). Willyamite from outcrop 3 penetrating arsenopyrite has zoning, visible in the BSE images (Text-fig. 6B). The parts of its grains in pyrite and close to chalcopyrite are lighter than that ones in arsenopyrite – this is caused by replacement of Sb by As (Sb 1.002, As 0.003 apfu and Sb 0.936, As 0.062, apfu, respectively (Table 4, items 17 and 18). Willyamite from outcrop 10 has low As admixtures from 0.005 to 0.006 apfu, but 0.001–0.002 Pb and Bi apfu was detected (Table 4, items 19 and 20) due to contemporary crystallization of the host minerals – galena and famatinite and the co-occurrence of the Bi minerals bismuthnite and aikinite. All the analyses of willyamite showed Se presence (0.038–0.113 wt. % i.e. 0.001–0.003 apfu, Table 4, items 17–20).

Berthierite $FeSb_2S_4$

The mineral called later berthierite was found by French mineralogist Pierre Berthier in an ore vein in a small abandoned mine at the village of Chazelles in Auvergne, France, and it was named haidingerite in honour of Wilhelm Karl Haidinger (Berthier 1827a). However, this name had already been given to another mineral (Berthier 1827b) and Haidinger (1827, see also Taylor and Phillips 1827) proposed the name berthierite to celebrate the mineral finder. The chemical composition of berthierite has been difficult to interpret (Sillwell 1926b) and this could be caused by changes of the mineral composition, because berthierite is stable over very limited intervals of fO_2 and fS (Williams-Jones and Normand, 1997). It is susceptible to chemical alterations especially caused by oxygen activity (Klimko *et al.* 2011). Berthierite occurs rather moderately frequently (c. 390 locations in all the world) and usually is a minor component of the Sb-bearing ores mostly as very small crystals; typical examples occur in the deposits of the Seinäjoki district, Finland (Borodaev *et al.* 1983), Sb-Au ore at the Jasenie area in the Lower Tatra Mts. (Čík *et al.* 2020), Sb ore at Wet Swine Gill, Caldbeck Fells, Cumbria (Fortey *et al.* 1984), Toyoha mine near Sapporo, Hokkaido (Ohta 1979) or polymetallic deposit Čumavići near Srebrenice, Bosnia (Radosavljević *et al.* 1990).

In Lower Silesia berthierite is known so far from the sulphide ores at Czarnów (Hoehne 1941; Mochnacka *et al.* 2009, 2015). In the investigated area it was found at the Wiciarka vicinity in outcrop 2, associated with four Sb minerals (stibnite, bournonite, geocronite and robinsonite) as well as with other ore ones (Table 1). Berthierite (orthorhombic *mmm*) forms euhedral crystals of the habit of thin rods, as in the group of 9 ones (2–3 mm long; Text-fig. 7A), partly ingrown in quartz. Its colour is gray with iridescent blue-violet-pinkish coating. Also inclusions of it in the shape of euhedral rods up to 0.2 mm long were found in pyrite and in bornite (Text-fig. 7B) as well as in galena, where it forms inclusions of short prism habits of the length up to 0.08 mm (Text-fig. 7C). The chemical composition of berthierite from this outcrop is typical: Fe 0.990 apfu, Sb 1.994 apfu and S 4.000 apfu; admixtures (Mn, Cu, Ag, Pb and As) are in the ranges from c. 0.02 to c. 0.11 wt. % (Table 5, item 1).

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* The name of the isle in the title of the cited paper was erroneously printed as "Sardina".

Mineral and location	No.	Fe	Mn	Sn	Zn	Cu	Ag	Pb	As	Sb	Bi	S	Se	Te	Σ, wt. %
Berthierite															
Outcrop 2	01	12.926	0.053			0.050	0.023	0.042	0.113	56.781		29.997			99.985
Boulangerite															
Outcrop 1	02	0.026		0.044		0.020		55.079	0.049	25.889	0.048	18.805	0.025	0.012	99.997
Outcrop 5	03	0.063				0.056		54.858	0.093	25.821		18.733	0.169	0.103	99.896
Outcrop 8	04	0.278		0.058	0.039	0.337		53.095	0.110	26.126	0.735	19.024	0.145	0.048	99.995
Outcrop 9	05	0.037		0.057	0.018	0.041		54.954	0.064	25.825	0.071	18.821	0.042	0.016	99.986
Bournonite															
Outcrop 1	06			0.293		12.980	0.176	42.150	1.115	23,265		19.750	0.146		99.877
Outcrop 2	07			0.142		13.114	0.112	42.713	2.109	21.817		19.922	0.061		99.992
Outcrop 4	08			0.069	0.068	13.097	0.158	43.085	3.298	20.040		20.016	0.099	0.053	99.983
Outcrop 6	09				0.040	12.976		42.436	0.169	24.663		19.697	0.016		99.999
	10			0.224	0.109	13.081	0.203	42.997	3.812	19.311		20.095	0.149		99.981
Outcrop 8	11				0.015	13.156	0.049	42.761	0.531	23.176	0.259	19.963	0.033		99.943
Outcrop 10	12				0.031	13.078	0.072	42.682	0.893	23.122	0.134	19.859	0.087	0.029	99.987
Chalcostibite															
Outcrop 1	13	2.092	0.110			23.068			0.422	48.313		25.707	0.222	0.051	99.985
Outcrop 3	14	1.820	0.066			23.417			0.271	48.533		25.748	0.127		99.982
	15	0.518			0.209	24.453	0.038	0.414	0.182	48.343		25.489	0.252	0.095	99.993
Outcrop 7	16	2.422				24.757			0.712	46.808		25.268			99.967
Outcrop 10	17	0.839	0.096*			24.791		0.248	0.369	48.931	0.167	24.417	0.099	0.042	99.999
Falkmanite															
Outcrop 1	18		0.038■			0.157		58.289	0.242	22.727	0.179	18.221	0.090	0.048	99.991
	19		0.079■			0.573		57.562	0.549	22.608	0.108	18.342	0.197	0.055	99.983
Outcrop 8	20		0.018■		0.035	0.103		58.528	0.299	22.544	0.040	18.246	0.067	0.009	99.989
Famatinite															
Outcrop 4	21	0.363			0.206	42.319			0.572	26.282	1.082	28.629	0.035		99,993
Outcrop 5	22	0.316			0.164	42.468	0.049		0.642	27.226	0.424	28.654	0.038		99.981
Outcrop 10	23	0.391			0,221	42.346	0.073		0.894	27.407	0.142	28.640	0.051	0.023	99.987
Geocronite															
Outcrop 2	24				0.093	0.253	0.039	65.218	0.162	16.462		17.543	0.188	0.021	99.979
Outcrop 4	25				0.017	1.513	0.015	64.729	1.958	14.576		17.146	0.023	0.016	99.993
	26				0.012	0.048	0.010	66.239	0.071	16.617		16.825	0.116		99.988
Robinsonite															
Outcrop 2	27	0.026			0.040	0.171		41.348	0.065	37.083	0.085	21.164			99.982
Outcrop 8	28	0.040			0.037	0.295	0.034	40.964	0.057	37.170	0.128	21.212	0.038	0.013	99.988
	29	0.097			0.104	0.410	0.110	40.266	0.078	37.350	0.182	21.314	0.058	0.017	99.986
Semseyite															
Outcrop 5	30	0.051				0.195	0.028	52.603	0.460	27.187		19.219	0.217	0.018	99.978
Outcrop 6	31	0.154				0.396	0.035	52.045	0.774	26.932		19.395	0.228	0.026	99.985
Tetrahedrite-(Fe)															
Outcrop 3	32	6.574			0.185	37.854	0.188	1.086	0.763	28.052	0.101	25.079	0.109		99.991
	33	6.520			0.239	37.036	1.409	1.272	1.678	26.517	0.138	25.030	0.142		99.989
Outcrop 4	34	6.640	0.029		0.055	37.683	0.369	1.173	0.969	27.670	0.176	25.037	0.124	0.062	99.987
	35	6.618	0.056		0.102	36.945	0.599	1.436	0.430	28.284	0.337	24.659	0.396	0.130	99.992

Crystallochemical formulae (apfu) calculated for (S+Sb+Te) atom amounts in the theoretical proportions (nos. 01–30) and for 6 atoms in the *A* site (nos. 31–34)

01: $(Fe_{0.990}Mn_{0.004}Cu_{0.003}Pb_{0.001}Ag_{0.001})_{\Sigma 0.999}(Sb_{1.994}As_{0.006})_{\Sigma 2.000}S_{4.000}$

02: $(Pb_{4.982}Fe_{0.008}Cu_{0.006}Bi_{0.004})_{\Sigma 5.000}(Sb_{3.982}As_{0.011}Sn_{0.007})_{\Sigma 4.000}(S_{10.992}Se_{0.006}Te_{0.002})_{\Sigma 11.000}$

03: $(Pb_{4.962}Cu_{0.017})_{\Sigma 4.979}(Sb_{3.976}As_{0.024})_{\Sigma 4.000}(S_{10.953}Se_{0.032}Te_{0.015})_{\Sigma 11.000}$

04: $(Pb_{4.734}Cu_{0.098}Fe_{0.092}Bi_{0.065}Zn_{0.011})_{\Sigma 5.000}(Sb_{3.964}As_{0.027}Sn_{0.009})_{\Sigma 4.000}(S_{10.959}Se_{0.034}Te_{0.007})_{\Sigma 11.000}$

05: $(Pb_{4.964}Cu_{0.012}Fe_{0.010}Zn_{0.005})_{\Sigma 4.998}(Sb_{3.977}As_{0.013}Sn_{0.009})_{\Sigma 3.999}(S_{10.988}Se_{0.009}Te_{0.003})_{\Sigma 11.000}$

06: $(Pb_{0.987}Sn_{0.012})_{\Sigma 0.999}(Cu_{0.991}Ag_{0.007})_{\Sigma 0.998}(Sb_{0.928}As_{0.072})_{\Sigma 1.000}(S_{2.991}Se_{0.009})_{\Sigma 3.000}$

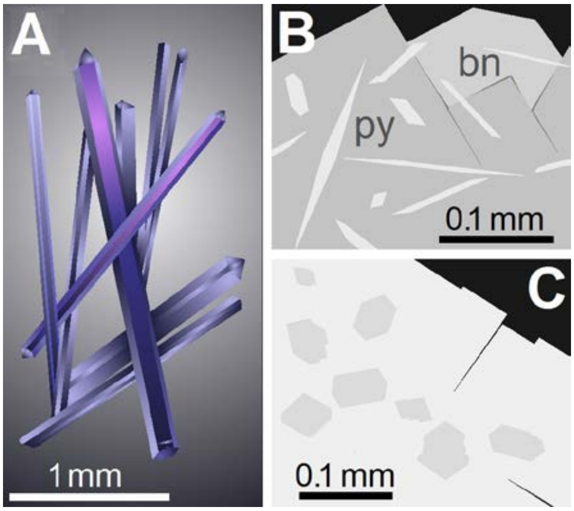
07: $(Pb_{0.993}Sn_{0.006})_{\Sigma 0.999}(Cu_{0.995}Ag_{0.005})_{\Sigma 1.000}(Sb_{0.862}As_{0.135})_{\Sigma 0.997}(S_{2.996}Se_{0.004})_{\Sigma 3.000}$

08: $(Pb_{0.997}Sn_{0.002})_{\Sigma 0.999}(Cu_{0.988}Ag_{0.007}Zn_{0.005})_{\Sigma 1.000}(Sb_{0.789}As_{0.209})_{\Sigma 0.998}(S_{2.992}Se_{0.006}Te_{0.002})_{\Sigma 3.000}$
09: $Pb_{1.000}(Cu_{0.995}Zn_{0.003})_{\Sigma 0.998}(Sb_{0.988}As_{0.011})_{\Sigma 0.999}(S_{2.999}Se_{0.001})_{\Sigma 3.000}$
10: $(Pb_{0.991}Sn_{0.009})_{\Sigma 1.000}(Cu_{0.982}Ag_{0.008}Zn_{0.007})_{\Sigma 0.997}(Sb_{0.756}As_{0.242})_{\Sigma 0.998}(S_{2.991}Se_{0.009})_{\Sigma 3.000}$
11: $(Pb_{0.993}Bi_{0.006})_{\Sigma 0.999}(Cu_{0.995}Ag_{0.002}Zn_{0.001})_{\Sigma 0.998}(Sb_{0.964}As_{0.033})_{\Sigma 0.997}(S_{2.998}Se_{0.002})_{\Sigma 3.000}$
12: $(Pb_{0.994}Bi_{0.003})_{\Sigma 0.997}(Cu_{0.993}Ag_{0.003}Zn_{0.002})_{\Sigma 0.998}(Sb_{0.941}As_{0.055})_{\Sigma 0.996}(S_{2.994}Se_{0.005}Te_{0.001})_{\Sigma 3.000}$
13: $(Cu_{0.901}Fe_{0.091}Mn_{0.005})_{\Sigma 0.997}(Sb_{0.985}As_{0.014})_{\Sigma 0.999}(S_{1.992}Se_{0.007}Te_{0.001})_{\Sigma 2.000}$
14: $(Cu_{0.914}Fe_{0.089}Mn_{0.003})_{\Sigma 0.996}(Sb_{0.991}As_{0.009})_{\Sigma 1.000}(S_{1.996}Se_{0.004})_{\Sigma 2.000}$
15: $(Cu_{0.962}Fe_{0.022}Zn_{0.007}Pb_{0.005}Ag_{0.001})_{\Sigma 0.997}(Sb_{0.993}As_{0.006})_{\Sigma 0.999}(S_{1.990}Se_{0.008}Te_{0.002})_{\Sigma 2.000}$
16: $(Cu_{0.988}Fe_{0.011})_{\Sigma 0.999}(Sb_{0.974}As_{0.022})_{\Sigma 0.996}S_{2.000}$
17: $(Cu_{0.951}Fe_{0.036}Co_{0.004}Pb_{0.003}Bi_{0.002})_{\Sigma 0.996}(Sb_{0.986}As_{0.012})_{\Sigma 0.998}(S_{1.996}Se_{0.003}Te_{0.001})_{\Sigma 2.000}$
18: $(Pb_{2.962}Cu_{0.025}Bi_{0.008}Hg_{0.002})_{\Sigma 2.997}(Sb_{1.964}As_{0.034})_{\Sigma 1.998}(S_{5.984}Se_{0.012}Te_{0.004})_{\Sigma 6.000}$
19: $(Pb_{2.895}Cu_{0.092}Bi_{0.005}Hg_{0.004})_{\Sigma 2.996}(Sb_{1.935}As_{0.062})_{\Sigma 1.997}(S_{5.969}Se_{0.026}Te_{0.005})_{\Sigma 6.000}$
20: $(Pb_{2.971}Cu_{0.016}Zn_{0.006}Bi_{0.002}Hg_{0.001})_{\Sigma 2.996}(Sb_{1.955}As_{0.040})_{\Sigma 1.995}(S_{5.990}Se_{0.009}Te_{0.001})_{\Sigma 6.000}$
21: $(Cu_{2.956}Fe_{0.028}Zn_{0.014})_{\Sigma 2.998}(Sb_{0.975}Bi_{0.021})_{\Sigma 0.996}(S_{3.964}As_{0.034}Se_{0.002})_{\Sigma 4.000}$
22: $(Cu_{2.962}Fe_{0.025}Zn_{0.010}Ag_{0.002})_{\Sigma 2.999}(Sb_{0.989}Bi_{0.008})_{\Sigma 0.997}(S_{3.960}As_{0.038}Se_{0.002})_{\Sigma 4.000}$
23: $(Cu_{2.951}Fe_{0.031}Zn_{0.015}Ag_{0.003})_{\Sigma 3.000}(Sb_{0.993}Bi_{0.003})_{\Sigma 0.996}(S_{3.955}As_{0.041}Se_{0.003}Te_{0.001})_{\Sigma 4.000}$
24: $(Pb_{13.744}Cu_{0.173}Zn_{0.063}Ag_{0.017})_{\Sigma 13.997}(Sb_{5.901}As_{0.095})_{\Sigma 5.996}(S_{22.887}Se_{0.105}Te_{0.008})_{\Sigma 23.000}$
25: $(Pb_{12.883}Cu_{0.983}Zn_{0.011}Ag_{0.007})_{\Sigma 13.884}(Sb_{4.938}As_{1.078})_{\Sigma 6.016}(S_{22.983}Se_{0.012}Te_{0.005})_{\Sigma 23.000}$
26. $(Pb_{13.951}Cu_{0.032}Zn_{0.008}Ag_{0.005})_{\Sigma 13.996}(Sb_{5.956}As_{0.041})_{\Sigma 5.997}(S_{22.907}Se_{0.093})_{\Sigma 23.000}$
27: $(Pb_{3.922}Cu_{0.052}Zn_{0.012}Fe_{0.009})_{\Sigma 3.997}(Sb_{5.992}Bi_{0.008})_{\Sigma 6.000}(S_{12.983}As_{0.017})_{\Sigma 13.000}$
28: $(Pb_{3.875}Cu_{0.090}Fe_{0.014}Zn_{0.011}Ag_{9.006})_{\Sigma 3.996}(Sb_{5.986}Bi_{0.012})_{\Sigma 5.998}(S_{12.794}As_{0.015}Se_{0.009}Te_{0.002})_{\Sigma 13.000}$
29: $(Pb_{3.785}Cu_{0.125}Fe_{0.034}Zn_{0.031}Ag_{9.019})_{\Sigma 3.994}(Sb_{5.983}Bi_{0.017})_{\Sigma 6.000}(S_{12.963}As_{0.020}Se_{0.014}Te_{0.003})_{\Sigma 13.000}$
30: $(Pb_{8.850}Cu_{0.106}Fe_{0.033}Ag_{0.008})_{\Sigma 8.997}(Sb_{7.784}As_{0.214})_{\Sigma 7.998}(S_{20.899}Se_{0.096}Te_{0.005})_{\Sigma 21.000}$
31: $(Pb_{8.676}Cu_{0.213}Fe_{0.095}Ag_{0.011})_{\Sigma 8.995}(Sb_{7.640}As_{0.356})_{\Sigma 7.996}(S_{20.894}Se_{0.099}Te_{0.007})_{\Sigma 21.000}$
32: $(Cu_{5.884}Pb_{0.087}Ag_{0.029})_{\Sigma 6.000}(Cu_{4.000}Fe_{1.953}Zn_{0.047})_{\Sigma 6.000}(Sb_{3.821}As_{0.168}Bi_{0.007})_{\Sigma 3.996}(S_{11.975}Se_{0.022})_{\Sigma 11.997}$
33: $(Cu_{5.681}Pb_{0.102}Ag_{0.217})_{\Sigma 6.000}(Cu_{3.998}Fe_{1.939}Zn_{0.061})_{\Sigma 5.998}(Sb_{3.614}As_{0.369}Bi_{0.011})_{\Sigma 3.994}(S_{11.975}Se_{0.022})_{\Sigma 11.997}S$
34: $(Cu_{5.849}Pb_{0.094}Ag_{0.057})_{\Sigma 6.000}(Cu_{3.996}Fe_{1.974}Zn_{0.014}Mn_{0.009})_{\Sigma 5.994}(Sb_{3.733}As_{0.215}Bi_{0.014})_{\Sigma 4.002}(S_{11.962}Se_{0.026}Te_{0.008})_{\Sigma 11.996}$
35: $(Cu_{5.791}Pb_{0.116}Ag_{0.093})_{\Sigma 6.000}(Cu_{3.942}Fe_{1.984}Zn_{0.026}Mn_{0.017})_{\Sigma 5.969}(Sb_{3.889}As_{0.096}Bi_{0.027})_{\Sigma 4.012}(S_{11.873}Se_{0.084}Te_{0.017})_{\Sigma 11.974}$

Table 5. Chemical composition of Sb sulphosalts, representative analyses; empty cells – component below detection limit (<~0.001 wt. %). * Co, ▪ Hg

Boulangerite $Pb_5Sb_4S_{11}$

The first known studies of the natural Sb components whose results became the basis of the chemical determination of the mineral later named boulangerite, were made by Rose (1829). A sample from Molières-Cavaillac in Le Vigan community, Gard department, France (presently the location of the type specimen of boulangerite), was analysed by Charles Louis Boulanger (1835a) and called *sulfure double d'antimoine et de plomb* or *Schwefel-Antimon-Blei* in the German version (Boulanger 1835b). Thaulow (1837) investigated another specimen of this mineral from Nasafjeld, the top of Kjølen Mt. (1,784 asl) in Lapland at the border between Norwegian Nordland and Swedish Westerbotten, and proposed for it the name *boulangerite*. Its chemical formula $3PbS{\cdot}Sb_2S_3$ calculated by Boulanger (1835a,b) was more or less accepted by Thaulow (1837), Hausmann (1839) and Rammelsberg (1839, 1846), but the latter in his handbook (Rammelsberg 1875, pp. 97–99) presented three possible formulae: $Pb_3Sb_2S_6$, $Pb_{10}Sb_6S_{19}$ and $Pb_5Sb_4S_{11}$. Then Sjögren (1897) confirmed the third one of the Rammelsberg's formulae as $5PbS{\cdot}2Sb_2S_3$ for the specimen from Sala silver mine (Sala silvergruva), in Västmanland County, Sweden. Shannon (1921) discussed the composition differences between a boulangerite specimen (probably from Independence mine, Wood River district, Idaho) and diaphorite; as a result of these and other considerations the formula $Pb_5Sb_4S_{11}$ is accepted at present. Some minerals like that called epiboulangerite



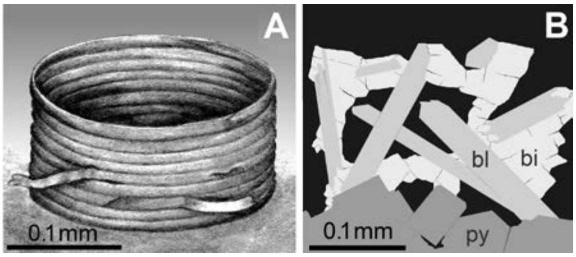
Text-fig 7. Berthierite, outcrop 2; A* – group of euhedral crystals, B – crystals overgrown by pyrite (py) and bornite (bn), C – crystals overgrown by galena, BSE images.

(Websky 1869, Shannon 1917) or mullanite (Shannon 1918a) were proved to be boulangerite (Shannon 1921) or its mixtures with other substances (see Berry 1940).

Boulangerite can be a significant component of sulphide-sulphosalt ore deposits such as in Bottino mine, Apuan Alps, Italy (Biagioni *et al.* 2018) or in Elisabeth mine, Gemerská Poloma, Slovakia (Števko and Sejkora 2021), of gold ores in Santa Comba-Fervenza region, Spain (Castroviejo 1990), in Awireth-Krinj, Pakistan (Gamerith 1990) or in Prestea mine, Ghana (Hammond and Tabata 1997) as well as of Pb-Zn-Ag sulphide ores in Janggun mine, S. Korea (Lee and Imai 1993) etc. Currently it has been reported from c. 1000 locations in all the world.

In Lower Silesia boulangerite is recognized in 9 occurrences of ore minerals (see Appendix 1). Moreover, from among the 10 locations investigated in this project, boulangerite was found in 4 ones (outcrops 1, 5, 8 and 9, see Table 1). It is associated with the Sb minerals: antimony, Sb-bearing domeykite, getchellite, stibnite, bournonite, chalcostibite and falkmanite (outcrop 1), stibnite, famatinite and semseyite (outcrop 5), falkmanite, bournonite, robinsonite and kermesite (outcrop 8), stibnite and kermesite (outcrop 9) and with Sb-free ore minerals (Table 1). Boulangerite crystals (monoclinic class *2/m*) usually are of rod, slat or hair habit, but sometimes slats form almost perfectly circular rings (see e.g. Caesar 1966 and Hanson *et al.* 1992). Such a ring was found in outcrop 5. It is 0.23 mm in diameter and 0.12 mm in height (Text-fig. 8A). The ring is formed from 9 circles of the boulangerite laths stacked on top of each other; in two circles the laths stick out from the ring's shape. In other outcrops the boulangerite crystals have subhedral to almost euhedral rod habits and are up to 0.5 mm long and c. 0.02–0.05 mm thick. Such crystals from outcrop 9 formed on pyrite and quartz, and they are in paragenesis with bismuthinite (Text-fig. 8B).

The amounts of the main chemical components in the studied boulangerite crystals are close to the theoretical contents and admixtures are low (Table 5 items 02–05). The percentage of Fe ranges from 0.026 to 0.278, Sn from <~0.001 to 0.058, Zn from <~0.001 to 0.039, Cu from 0.020 to 0.337, As from 0.049 to 0.110; only Bi is higher (0.735) in the specimen with bismuthinite, in other ones only from <~0.001 to 0.071 in wt. %. It is worth noting that Se and Te are present in all the analysed grains from 0.025 to 0.160 and from 0.012 to 0.103 wt. %, respectively. Zonality in chemical composition inside the crystals was not observed, maybe due to their small size. When the chemical analyses were recalculated to the formulae, the main components had only slightly lower contents in apfu than theoretical values, excepting the sample with bismuthinite in paragenesis from outcrop 8 (see formulae list in Table 5). For the associate ore minerals see Appendix 2 and for their crystallochemical formulae – Appendix 3.



Text-fig 8. A* – Boulangerite of ring-shaped habit, formed by circles of lath crystals, outcrop 5. B – Boulangerite (bl) with bismuthinite (bi) and pyrite (py), outcrop 9, BSE image.

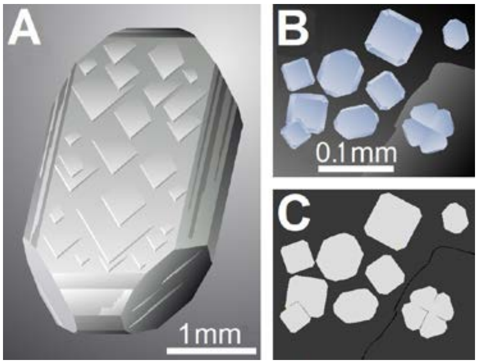
Bournonite $PbCuSbS_3$

The kind of Sb ore that was the source of the mineral named bournonite, was called in the past *Spißglantz* (Albinus 1590), *Radel Erz* and *Schwarzspiesglaßerz* (Bonnard 1815) or *Spiesglansbleyerz* (Berzelius 1821 p. 189). Its samples sometimes contained euhedral orthorhombic crystals (pyramidal class *mm2*), and thus were readily included in collections; probably the first description of such a specimen, collected in the mine Huel Boys near Endellion, Cornwall county, with excellent drawings of the crystals was published by Rashleigh (1797, plate XIX fig. 2 and drawings *a* and *b*). Analysis of the chemical composition of this specimen was made by Hatchett (1804), who called it *triple sulphuret of lead, antimony and copper*. The precise characteristic of this mineral with use of this name and extensive genetic considerations may be found in Bournon's (1804) article. The new mineral was also included to the mineralogical handbook published by Jameson (1805, pp. 579–582), who proposed the name *bournonite*. But Bournon (1813) used the name *endellione* in his own collection of minerals as well as for specimens in other collections (e.g. Bournon 1817, pp. 409, 411 and 417); Allan (1834, p. 265) applied the English version *endellionite*. A geological description of the ore-bearing veins (with bournonite) from Cornwall, including those from the mine Huel Boys, was published by Phillips (1814, pp. 29–30). The method of bournonite identification by chemical analysis was proposed by Berzelius (1821, pp. 189–190 and 198–199).

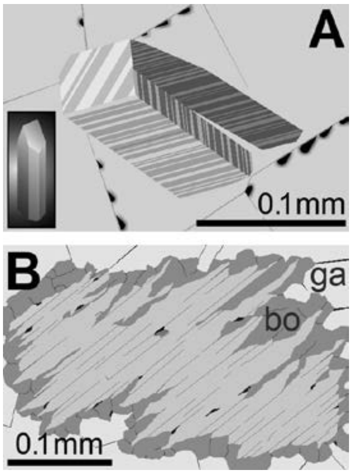
The number of the presently known bournonite occurrences on the whole Earth may be estimated at c. 1300. This mineral is a typical component of sulphide-sulphosalt metasomatic impregnation or vein ores as e.g. in Harz area, Germany (Bonnard 1815), Madenbelenitepe in Bursa province, Türkiye (Çağatay *et al.* 1979), Baia Mare area, Romania (Damian and Damian 2003), Mária Margita deposit in Ochitná area, Slovakia (Števko *et al.* 2009), Srebrenjak Brok area, Croatia (Jurković 1959) or stratabound Kuroko deposits, Japan (Yamaoka *et al.* 1983). It is frequently a component of gold-bearing ores, e.g. in Prestea mine, Ghana (Hammond and Tabata 1997).

In Lower Silesia up to now bournonite has been found in 14 locations (Appendix 1); this number does not include those investigated in this project which were found in outcrops 1, 2, 4, 6, 8 and 10. Bournonite in the samples from these outcrops is subhedral and less often euhedral. An almost perfect crystal c. 5 mm long was found in outcrop 1 (Text-fig. 9A). Its colour is typically gray, the faces have few stripes and the face (001) has slightly protruding thin plates outlined by the edges [110]. The stripes and the blocky face (001) suggest unstable physical conditions of crystallization. A sample with a group of small euhedral crystals of bournonite (0.03–0.08 mm) on quartz was found in outcrop 10 (Text-fig. 9B). Their habit is platy with the main (001) face. They have a bluish coating, but after polishing their colour is gray. A twin of four crystals with repeated contact on (110) occurred in this sample and the twinning was visible exactly on the natural surface and in the BSE image after polishing of the crystals (Text-fig. 9C). Both individual crystals from this outcrop and the twin are very similar to those described (and drawn) from the Rashleigh's (1797) collection. An example of a subhedral crystal partly transformed into a submicroscopic mixture of several sulphide minerals with very small (≤0.08 mm) antimony inclusions was collected in outcrop 4 (Text-fig. 3). Moreover, an aggregate of subhedral bournonite grains smaller than 0.1 mm displaced falkmanite and galena in a specimen from outcrop 8 (Text-fig. 10B). The size of the bournonite crystals usually is small or very small, from few millimetres to tenths of millimetre, like in the specimens from the investigated outcrops described here. However, crystals up to 3 cm long were found in the mines at Park City, Utah (Horn and Hunt 1915).

The chemical composition of the analysed bournonite is rather stable in crystals from the same veinlet and significant zoning in them was not found. Distinct differences appeared between bournonite samples from various outcrops in the contents of the admixture elements (Table 5 items 06–12). Most variable are admixtures of As (0.169–3.812 wt. %; 0.011–0.242 apfu); it is worth noting that these limit values were found in bournonite from the same outcrop 6 but each in crystals in one of the two different veinlets (items 14 and 15). In bournonite from other 5 outcrops the As contents (0.531–3.298 wt. %; 0.033–0.209 apfu) are within the above limits. These data, especially from outcrop 6, distinctly suggest strictly local physical-chemical conditions of formation of the studied Sb-bearing associations of minerals. This proposed interpretation is supported by changes of the contents of other admixtures (in wt. %): Sn <~0.001–0.293, Zn <~0.001–0.109, Ag <~0.001–0.203, Bi <~0.001–0.259, Se 0.016–0.149 and Te <~0.001–0.053; Bi and Te were found only in two samples.



Text-fig 9. A* – Bournonite euhedral crystal, outcrop 1. B* – Bournonite on quartz, lower left twin of four crystals, C – same, BSE image of the specimen after polishing, outcrop 10.



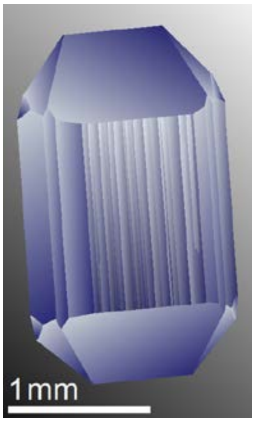
Text-fig 10. A – Falkmanite grains with polysynthetic twins overgrown by galena, reflected light photomicrograph, nicols obliquely crossed, insert* – euhedral crystal of falkmanite 1.8 mm long, outcrop 1. B – Falkmanite partly replaced by bournonite (bo), ga – galena, outcrop 8, BSE image.

Chalcostibite $CuSbS_s$

Initially also to specimens of this mineral were given various names, depending on the diverse occurrences in which they were found. Long ago chalcostibite was included most probably into a group of Sb-bearing ores called *Spießglaß-Ertz*, maybe those ones which were linked also with Cu and S compounds i.e. *Kupffer-Kieße* (see e.g. Henckel 1725, p. 415). The specimens from the ore vein in Graf Jost-Christian mine near Wolfsberg castle, Mansfeld-Südharz district, Germany, were described as a new mineral *Kupfer-Antimonglanz* (Zincken 1835); its chemical composition was determined by Rose (1835). The name of this chemist became the basis for calling this mineral *rosite* (Huot 1841, p. 197), however Glocker (1847, p. 32) translated the German name to the Latinised form "chalcostibites" with use of the Greek words *χαλκὸς* (chalkos, copper) and (*στίβι*, antimony); this name was commonly accepted. *Wolfsbergite* (Nicol 1849, pp. 484–485) and *guejarite* (Cumenge 1879) were other proposals of the new mineral's name, but Penfield and Frenzel (1897) proved the identity of these minerals with chalcostibite.

Till now nearly 200 chalcostibite occurrences have been recognized across the entire Earth's surface. This mineral may be e.g. a component of sulphide-sulphosalt Sb deposits like those at Dve Vody and Dúbrava in Nízké Tatry Mts., Slovakia (Hak *et al.* 2020), sulphide-carbonate veins with Sb minerals as in Goesdorf, Luxembourg (Philippo and Hanson 2007), uranium-base metal mineral accumulations as in the Příbram ore district, Czechia (Škácha *et al.* 2015) or Au-Sb mineralization in the Maltan deposit, Russia (Fridovsky *et al.* 2014).

Information on the finding of chalcostibite in Poland is not available, thus probably its occurrence in the investigated area in outcrops 1, 3, 7 and 10 is the first one. It is in association or in paragenesis (Table 1) of the Sb minerals but not the same in all outcrops; with: antimony (outcrop 1), Sb-bearing domeykite (1, 3), getchellite (1, 7), stibnite (1, 3, 7), willyamite (3, 7), boulangerite (1), bournonite (1, 10), falkmanite (1), famatinite (10), tetrahedrite-(Fe) (3), cervantite and schafarzikite (both in 7). Similarly, assemblages of other ore minerals are diverse (Table 1). The variable associations indicate to some scale different conditions of origin in each outcrop. The crystals of chalcostibite (orthorhombic, class *mmm*) are short prismatic euhedral (Text-fig. 11) or subhedral (Text-fig. 5), their size ranges from 0.2 to 2.7 mm. They contain variable amounts of admixtures (Table 5 items 13–17), namely Fe (0.518–2.422 wt. %; 0.011–0.091 apfu), Pb (<~0.001–0.414 wt. %; ≤0.005 apfu), As (0.182–0.712 wt. %; 0.06–0.022 apfu), Se (<~0.001–0.252 wt. %; ≤0.008 apfu). Moreover, Mn, Co, Zn, Ag, Bi and Te are minor admixtures, present selectively only in few or one analysed crystal. Almost all the chalcostibite grains were homogeneous and their analyses are representative for the whole crystals. Only in outcrop 3 had one crystal two growth zones .The inner part (Table 5 item 14) had typical admixtures of Fe, As and Se plus a low one of Mn, but with a very thin and discontinuous outer zone with a low admixture of Fe and Pb containing also minor amounts of Zn, Ag and Te admixtures (Table 5 item 15). Two other little chalcostibite grains in the same sample were of very similar composition (analyses not listed in Table 5). This suggests a change of the physical-chemical conditions at the end of chalcostibite crystallization in this outcrop.



Text-fig 11*. Euhedral chalcostibite with striae parallel to the C axis in the faces of the pinacoid (100) and blue oxidation coating, outcrop 7.

Falkmanite $Pb_3Sb_2S_6$

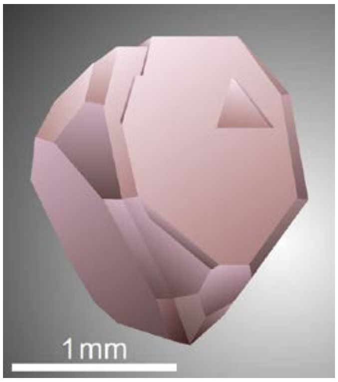
This was described as a new mineral by Hiller (1939) as well as by Ramdohr and Ödman (1940) in specimens from Boliden mines, Sweden, and Bayerland mine in the Waldsassen area, Germany; its name refers to Oscar Carl August Falkman, the general director of the Boliden mines. Moreover Hiller (1939) laid emphasis on the similar and different features of falkmanite and boulangerite. But Robinson (1948a) suggested the sameness of these two minerals. Nevertheless e.g. the conclusion of McQueen's (1987) studies supported the idea that falkmanite is an individual mineral. It was included in the formal list of the Pb-Sb sulphosalts although with some doubts (Moello *et al.* 2008). Falkmanite was described independently from co-occurring boulangerite in the epithermal El Cobre vein of the Guerrero Ag-Pb-Zn mine, Taxco district, Mexico (Hynes 1999). It was also found in the Pb-Bi-(Ag)-Te-Cu, Pb-Sb-(As), Sb-Cu-(Ag, Fe, Zn) sulphosalt assemblages of the Boranja deposits, Podrinje district, Serbia (Radosavljević *et al.* 2013), in Pb-Zn-Ag polymetallic ores of Bianjiadayuan deposit, Inner Mongolia, China (Wang *et al.* 2014) and in Plaka area veins with ores of Mo, W, Pb, Zn, Cu, As, Sb, Bi and Ag in Lavrion, Greece (Voudouris *et al.* 2008). From around the world only c. 20 locations of falkmanite have been reported; this may be connected with its resemblance to boulangerite and thus with problems of identification.

The present authors did not find any information on the occurrence of falkmanite in Poland, and probably this is the first mention of it. This mineral was identified in two outcrops: 1 and 8; the associated Sb minerals are: antimony, Sb-bearing domeykite, getchellite, stibnite, boulangerite, bournonite and chalcostibite in outcrop 1 and boulangerite, bournonite, robinsonite and kermesite in outcrop 8. In outcrop 1 a euhedral crystal (monoclinic, class not recognized) 1.8 mm long was found (insert in Text-fig. 10A). Moreover, its grains occurred as inclusions up to 0.15 mm in size in galena (Text-fig. 10A). These grains had polysynthetic twinning in the form of parallel slats up to 0.01 mm thick. The specimen from outcrop 8 contains a group of falkmanite parallel slabs with distinct cleavage surrounded by galena. But along the contact of these two minerals bournonite crystallized, replacing both of them, as shown by the well recognizable traces of etching (Text-fig. 10B). Probably this process was the result of inflow of the Cu-bearing solution, that reacted chemically with the two earlier formed minerals, which contained only c. 0.1 (falkmanite) and c. 0.6 (galena) wt. % Cu (see Table 5 and Appendix 2). Similar replacement of falkmanite by bournonite was described in the specimen from Bayerland mine (Mozgova *et al.* 1983). Admixtures to the main elements of the falkmanite chemical composition are rather moderate: Cu 0.103–0.573 wt. % (0.016–0.092 apfu), As 0.242–0.549 wt. % (0.034–0.062 apfu), Bi 0.40–0.179 wt. % (0.002–0.008 apfu), Se 0.067–0.197 wt. % (0.009–0.026 apfu), moreover minor amounts of Hg, Zn, and Te were determined (Table 5, items 18–20).

Famatinite Cu_3SbS_4

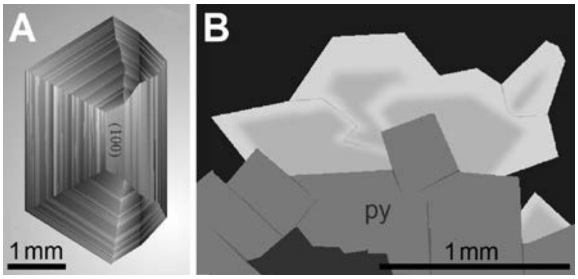
In ore specimens from so called enargite veins exploited in the mines Mejicana-Verdiona, Mejicana-Upulungos and Anduesa-Mejicana (Argentinean province La Rioja, Famatina mountain ridge, west of the town of Famatina) a mineral at that time unknown was found by Stelzner (1873, pp. 240–243), who investigated it and named *famatinite*. After finding other minerals similar to this one a discussion appeared on doubts concerning their identity (or not) with famatinite, e.g. next year Weisbach (1874) published an article on a new mineral which he named luzonite and he discussed its similarity to famatinite. Gaines (1957) analysed the structures and chemical composition of this related group of minerals and concluded that famatinite is a member of the $Cu_3(As,Sb)S_4$ series.

Presently all over the Earth c. 210 mineral occurrences with the presence of famatinite have been described, e.g. in Au-Ag-Te ores at Săcărâmb, Romania (Dincă 2019) or in polymetallic mineralization of the Shin-Ohtayo deposit on Hokkaido, Japan (Imai *et al.* 1999). In Poland it was mentioned from the Miedzianka deposit in Lower Silesia (see Appendix 1) and found in the Lubin-Sieroszowice orebody (Kucha 2007, Piestrzyński and Pieczonka 2012). In the area of the present studies famatinite was found in outcrops 4, 5 and 10. In outcrop 4 it was associated with the Sb minerals: antimony, bournonite, geocronite, and tetrahedrite-(Fe), in outcrop 5 – with stibnite, boulangerite and semseyite and in outcrop 10 – with willyamite, bournonite and chalcostibite. For other ore minerals in these outcrops see Table 1. A few famatinite crystals (tetragonal class $\overline{4}\ 2m$) from outcrop 4 of size up to 2.2 mm and of euhedral (tetrahedral+scalenohedral) habits formed intergrowths with parallel *A* axes, sometimes with small windows on the tetrahedron faces (Text-fig. 12). A subhedral famatinite grain from outcrop 10 contained inclusions of willyamite in one growth zone (Text-fig. 6C); the specimen from outcrop 5 comprised several anhedral famatinite



Text-fig 12*. Intergrowth of euhedral crystals of famatinite, one face is with small window, outcrop 4.

grains 0.2–0.4 mm in size as inclusions in quartz. All the analysed specimens (Table 5 items 21–23) contained chemical admixtures of Fe (0.316–0.391 wt. %, 0.025–0.031 apfu), Zn (0.164–0.221 wt. %, 0.010–0.015 apfu), As (0.572–0.894 wt. %, 0.034–0,041 apfu), Bi (0.142–1.082 wt. %, 0.003–0.021 apfu) and Se (0.035–0.051 wt. %, 0.002–0.003 apfu). Moreover, in famatinite from outcrops 5 and 10 Ag was found (0.049–0.073 wt. %, 0.002–0.003 apfu) and from outcrop 10 – Te (0.023 wt. %, 0.001 apfu). Zoning of the chemical composition in crystals was not detected, but some differences occur between samples from various outcrops in the contents of admixtures, thus also of the main components.



Text-fig 13. A* – Geocronite, crystal of euhedral habit and with polysynthetic twinning, the face (100) is parallel to the image plane, outcrop 2. B – Geocronite, the inner darker zone of the crystals is richer in As and Cu admixtures than the outer one, py – pyrite, outcrop 4; BSE image.

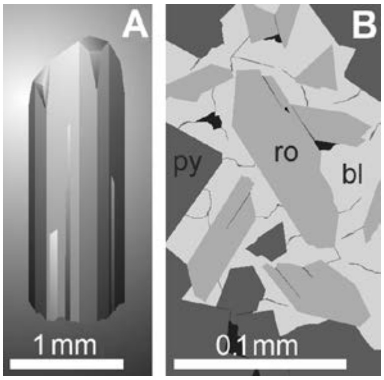
Geocronite $Pb_{14}Sb_6S_{23}$

A mineral from Sala silver mine, Sala district, Västmanland county, Sweden, which was thought to be identical with *Weiſsgültigerz* (tetrahedrite or freibergite), after verification was recognized to be something different (Svanberg 1840, 1841). Moreover, this scientist found the same mineral in ore from Torgschakts mine and from the exploited exposure Knut in the same district. After investigation he named it as a new mineral *geocronite* (Svanberg 1840, 1841) from the Greek words γή (ge, Earth) and κρόνος (Kronos in ancient Greece i.e. Roman god Saturnus, hence the planet name Saturn); in alchemy antimony and lead were symbols of Earth and Saturn, respectively. A little later Apjohn (1841) described a new mineral from Kilbricken lead mine in Clare county, Ireland, but Prior (1902) demonstrated its identity with geocronite. A good example of the occurrence of geocronite with 7 other Pb-Sb sulphosalts in the Apuan Alps, Italy, was presented by Biagioni *et al.* (2016) or in addition with 18 Sb sulphides and sulphosalts from Casualidad mine in Almeria, Spain, by Rewitzer *et al.* (2019), the latter with interesting BSE images of the geocronite-bearing parageneses. The total number of all presently known occurrences of geocronite is c. 160, but probably there is only one in Poland, in the Miedzianka ore field, Lower Silesia (Hoehne 1953).

In this study geocronite was found in two outcrops: 2 and 4. In the first of them it is associated with the Sb minerals: stibnite, berthierite, bournonite and robinsonite, in the second one – with antimony, bournonite, famatinite and tetrahedrite-(Fe); for the co-occurring other ore minerals see Table 1. Geocronite crystals (monoclinic, class *2/m*) are euhedral to subhedral, but incidentally with specific features. The specimen from outcrop 2 (Text-fig. 13A) c. 4 mm long probably formed under unstable and anisotropic physical conditions and this caused different faces in positive and negative directions of the *B* axis (horizontal in the picture plane) and polysynthetic twinning of thin (100) laminae. However, it has practically the same chemical composition in the whole volume (for representative analysis see Table 5 item 24). The admixture contents were moderate: Cu c. 0.25 wt. % (0.17 apfu), Zn c. 0.09 wt. % (0.06 apfu), Ag c. 0.04 wt. % (0.02 apfu), As c. 0.16 wt. % (0.10 apfu), Se c. 0.19 wt. % (0.10 apfu), Te c. 0.02 wt. % (0.01 apfu). A group of euhedral geocronite crystals from outcrop 4 (Text-fig. 13B) 0.3–0.9 mm in size arose on pyrite druse. The crystals have distinct zoning caused by a difference in chemical composition, see Table 5 items 25 (inner zone) and 26 (outer zone). The contents of main admixtures in the inner zone were high, e.g. Cu c. 1.5 wt. % (0.98 apfu) and As c. 2.0 wt. % (1.08 apfu); this had the effect of lower presence of the main components (Sb c. 14.6 wt. %, 4.94 apfu and Pb c. 64.8 wt. %, 12.88 apfu). In the outer zone these elements were in the contents: Cu c. 0.05 wt. % (0.03 apfu), As c. 0.07 wt. % (0.04 apfu), Sb c. 16.2 wt. % (5.96 apfu) and Pb c. 66.24 wt. % (13.95 apfu). Most probably in this case chemical (or physical-chemical) conditions during crystallization (apparently composition of the parent fluid) changed.

Robinsonite $Pb_4Sb_6S_{13}$

A specimen of this sulphosalt was first recognized in the sample found in 1943 at the Red Bird mine, Pershing County, Nevada, by Edgar H. Bailey (Berry *et al.* 1952). Moreover, it was determined by these authors to be identical to one of the substances obtained through laboratory synthesis by Robinson (1948b). Thus Berry *et al.* (1952) concluded they had



Text-fig 14. A* – Robinsonite, a part of a euhedral crystal, outcrop 2. B – Robinsonite (ro), subhedral crystals in paragenesis with boulangerite (bl) and pyrite (py), outcrop 8; BSE image.

discovered a new mineral and named it *robinsonite*. Further considerations on the composition of robinsonite and this mineral's structural features were published by Jambor (1967) in his study of the Pb-Sb-S-As minerals from Madoc-Sharbot Lake area, Ontario and by Ayora and Gali (1981) who investigated As-(Bi-Au-Cu)-Sb ore from veins of the Vall de Ribes in Eastern Pyrenees, Spain, and moreover by Makovicky *et al.* (2004) in their research of robinsonite from Malé Železné deposit, Nízke Tatry Mts., Slovakia. Probably the first occurrence of robinsonite in the British Isles as one of the seven Sb sulphides and sulphosalts in the ores of Blwch mine, Deganwy area, Wales was described by Bevins *et al.* (1988). The occurrence of this mineral as a primary component of ores in Jáchymov district was characterized by Ondruš *et al.* (2003). At least 50 locations of robinsonite have been recognized till now all over the Earth, but apparently none in Poland.

In the area currently investigated by the authors robinsonite specimens were found in outcrop 2 with the Sb minerals: stibnite, berthierite, bournonite, geocronite and in outcrop 8 with boulangerite, bournonite, and falkmanite (Table 1). These crystals of robinsonite (monoclinic class *2/m*) had eu- or subhedral prismatic habits and a length of 2.5 mm (outcrop 2; Text-fig. 14A) or up to 0.11 mm (outcrop 8; Text-fig. 14B). The specimen from outcrop 2 is an exactly parallel growth of several crystals of essentially the same chemical composition (representative analysis see Table 5 item 27). Admixtures are low: Fe c. 0.03 wt. % (0.01 apfu), Zn c. 0.04 wt. % (0.01 apfu), Cu c. 0.20 wt. % (0.05 apfu), As c. 0,05 wt. % (0.02 apfu), Bi c. 0.08 wt. % (0.01 apfu). In outcrop 8 robinsonite, found in two nests in quartz, occurs in both cases in paragenesis with anhedral boulangerite between groups of subhedral pyrite. Robinsonite, partly almost euhedral, crystallized here on pyrite and the space between crystals of these two minerals was filled by boulangerite. The chemical composition of robinsonite varies slightly between the two nests (Table 5 items 28 and 29), e.g. in contents of Pb (40.96 wt. %, 3.88 apfu) vs 40.27 wt. %, 3.79 apfu). As admixtures, there appeared Ag (0.05–0.11 wt. %), Se (0.04–0.06 wt. %) and Te (0.01–0.02 wt. %). Thus the migration of the chemical elements to the mineral formation spaces differed not only between these two outcrops, but also for the two nests of outcrop 8.

Semseyite $Pb_9Sb_8S_{21}$

Semseyite was recognized as a new mineral from the ore deposit Felsőbányá*, Hungary (now Baia Sprie* in Romania) by Krenner (1881) and named to honour the Hungarian collector of minerals Andor Semsey. However, it is possible that the Pb-Sb-S mineral(s) called *Federerz* and included by Rose (1833) in one group with bournonite, plagionite and zinkenite, could in some cases have been semseyite. Spencer and Prior (1899) formally established the group: plagionite, heteromorphite and semseyite. Specimens of semseyite from the mine at Glendinning in Eskdale, Scotland, were very well investigated and compared with plagionite by Smith and Prior (1919). The occurrence of semseyite in the polymetallic ore deposit Bohutín in the Příbram area (Litochleb *et al.* 2008) is a good example of the geological situation and paragenesis of this mineral. Till now c. 180 locations of semseyite have been recognized all over the world, but apparently not in Poland.

In the area of the current investigation semseyite was found in samples from two outcrops (5 and 6). The associated Sb minerals are stibnite, boulangerite and famatinite in outcrop 5, stibnite and bournonite in outcrop 6 (Table 1). A euhedral crystal of semseyite (monoclinic, class *2/m*) with a blue-grayish coating was c. 3 mm long (outcrop 5; Text-fig. 15A). The striae parallel to the *C* axis on the {hk0} faces and spots on the {hkl} and { } faces refer to the simultaneous parallel growth of many individual parts of the crystal. The chemical composition is practically the same in its whole volume and the main admixtures are Cu (c. 0.2 wt. %, 0.01 apfu), As (c. 0.5 wt. %,

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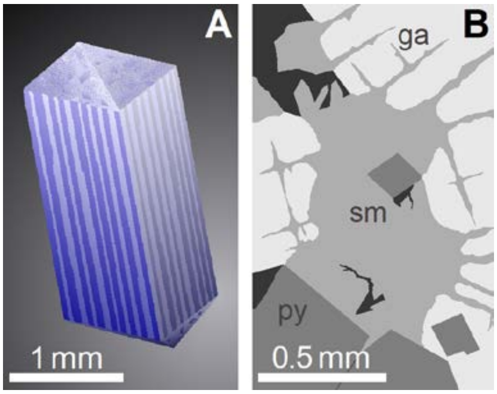
* The Hungarian name means Upper Mine like the old Romanian name Baia de Sus; Baia Sprie from Romanian *aspriu, asprie*, its source in Greek *άσπρος* (*aspros* i.e. white) in sense silver, silver coin, thus Mine of Silver.



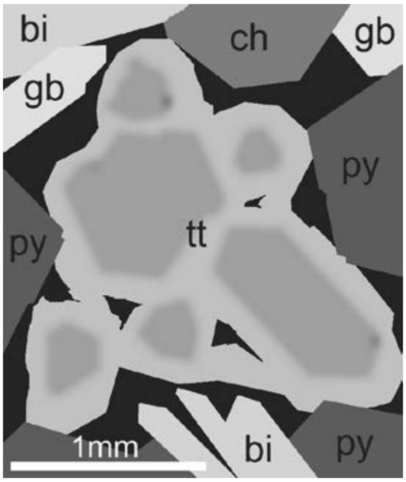
Text-fig. 15. A* – Semseyite, euhedral crystal with ribbed faces parallel to the C axis, the blue color is caused by iridescent surface, outcrop 5. B – Semseyite (sm) replacing galena (ga) along its cleavage and partly occurring as euhedral crystals, py – pyrite, outcrop 6; BSE image.

0.21 apfu) and Se (c. 0.2 wt. %, 0.10 apfu); c. 0.03 wt. % (c. 0.01 apfu) Ag is present as well (Table 5 item 30). In outcrop 6 eu- or subhedral semseyite crystals were found as well, but mostly this mineral occurs as a homogeneous mass replacing galena initially along the cleavage planes and then in its whole volume. Pyrite co-occurring with galena remains stable (Text-fig. 15B). This indicates that after galena and pyrite formation a new solution containing Sb appeared and used Pb from galena to become the parent medium for semseyite. The chemical composition of semseyite is stable in its whole volume as well, but the contents of some admixtures are higher than in the specimen from outcrop 5, namely: Cu c. 0.40 wt. %, 0.02 apfu, As c. 0.80 wt. %, 0.36 apfu (Table 5 item 31).

Tetrahedrite-(Fe) $Cu_6(Cu_4Fe_2)Sb_4S_{12}S$

A component of Cu ores exploited for a very long time, not rarely bearing also Ag, thus described by Agricola (1561) as *argentum rude album**, but commonly the name *Fahlertz*** or *Fahlerz* was used (see e.g. Henckel 1725); more synonyms were listed by Haditsch and Maus (1974). The name “tetrahedrite” was proposed by Haidinger (1845) because of the tetrahedral habit of its crystals. Tetrahedrite subgroup minerals are very common as a component of various ores, frequently polymetallic ones; at least 6600 locations are known all over the Earth. Also in Lower Silesia many occurrences could be listed (see Appendix 1).

However, in the investigated area this mineral occurred only in two locations: outcrop 3 – in association with the Sb-bearing domeykite, stibnite, willyamite, and chalcostibite, and 4 – with antimony, bournonite, famatinite and geocronite (Table 1). The tetrahedrite-(Fe) crystals (isometric, class $\overline{4}\ 3m$) are subhedral, ≤1.3 mm in size and form groups. They have cores and outer rims of different chemical composition (Table 5 items 32 and 34 – cores, 33 and 35 – rims). In the sample from outcrop 4 (Text-fig. 16) the contents of some elements varied as follows in core and in rim, respectively: Cu 37.68 and 36.95 wt. % (5.85 and 5.79 apfu), Pb 1.17 and 1.44 wt. % (0.09 and 0.12 apfu), Sb 27.67 and 28.28 wt. % (3.73 and 3.89 apfu), Bi 0.18 and 0.34 wt. % (0.01 and 0.03 apfu), As 0.97 and 0.43 wt. % (0.22 and 0.10 apfu), Se 0.12 and 0.40 wt. % (0.03 and 0.08 apfu). But within cores and rims the contents of the elements were stable. This is another example of changes of the physical-chemical conditions during crystallization of the investigated mineral parageneses.



Text-fig. 16. Zoned tetrahedrite (tt) in paragenesis with bismuthinite (bi), chalcopyrite (ch), galenobismutite (gb) and pyrite (py), outcrop 4; BSE image.

Cervantite $Sb^{3+}Sb^{5+}O_4$

This substance is an oxidized component of Sb ores used since ancient antiquity, but for long time it was not exactly separated and identified as a single mineral. One of the earliest descriptions of the antimony oxides called it *antimoine colorė blanc* and classified as *muriate d’antimoine* i.e. Sb chloride be-

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* In Latin white ore of silver. ** In German Fahl – pale (colour), ertz or erz – ore.

cause of their reaction with hydrochloric acid (l'acide muriatique). This description was published in a collection catalogue of minerals with characteristics of the occurrence locations in Přibram, Czechia and in Malazka, Hungary, now Malacky, Slovakia (Born 1790, pp. 147–150). Emmerling (1796, pp. 480–483) named the Sb oxide ores *Weiß-Spiesglaserz* and mentioned that their colour may be white or off-white but also yellowish, straw-yellow or grayish of various intensity. Haüy (1801, p. 274) confirmed that *antimoine oxydė* may be not only white, but yellow as well. Probably this encouraged Breithaupt (1823 p. 98) to introduce the name *Gelbantimonerz* (yellow antimony ore) for this mineral. Apparently not pure Sb oxide minerals but maybe mainly cervantite and valentinite mixtures in various proportions with other components Beudant (1832, pp. 615–616) divided into two groups: *exitèle* (ἐξίτηλος, exítêlos – in Greek "that of lost colour", "colourless" with synonyms *oxide d'antimoine cristallisé*, *antimoine oxidé*, *antimoiné blanc*, *chaux d'antimoine*; *antimoine muriaté*, *Antimonblüthe*, *Weissspiesglanzerz*, *Spiesglanzweiss*) and *stibiconise* (conic antimony, with synonyms *antimoine oxidé terreux*, *acide antimonieux*, *Antimonocker*, *Spiesglanzocker*). He noted that the second one may form as a yellowish or yellow-grayish cover on Sb sulphides. Dufrénoy (1845, pp. 653–655) presented the names: *antimoine oxydé* (*antimoine blanc*, *chaux d'antimoine*, *Antimonblüthe*, *exitèle*, *antimonphyllite*) and *acide antimonieux* (*antimoine oxydé terreux*, *stibiconise*, *Antimonocker*, *Speissglanzocher**); some could be related to cervantite only in part. Moreover Dufrénoy (1845) wrote that he had found a mineral at Chazelles in Auvergne, France, reportedly very similar to the type specimen (the latter not preserved till now) collected by Angel Valejo at Cervantes in Galicia, Spain. Apparently for the first time the name *cervantite* was published by Dana (1850, p. 417). The structure of cervantite was presented by Natta and Baccaredda (1933), however the existence of cervantite was rejected by Vitaliano and Mason (1952). Nevertheless Gründner *et al.* (1962) discussed the redefinition of cervantite as a mineral species with a positive conclusion. But the problem has not been solved, because the extensive studies of the yellow ochres from Cervantes and Brasina (called *historical antimony ochres*) done by Garcia-Guinea *et al.* (2023) in fact did not support an opinion about the existence of cervantite, maybe only in this area. The Sb oxide compounds were studied by Gopalakrishnan and Manohar (1974) and confirmed the distinction of cervantite. The publications on Sb ore deposits usually only mention the occurrence of cervantite (e.g. Davis *et al.* 1986) or contain its very general description (e.g. Boev *et al.* 2012) probably due to the problems with its research. However, the existence of cervantite is presently formally accepted, essentially on the basis of the studies of Gründner *et al.* (1962). It is possible that doubts appeared due to the uncertain type specimen and problems with its identification in mixtures of Sb oxide compounds in natural samples. The number of the presently noted occurrences all over the Earth is c. 360 but many of them may involve uncertain identification of this mineral. In Poland it has not been identified untill now.

Text-fig. 17*. Cervantite of platy and lath habits on a face of quartz crystal, outcrop 7.

In the studied area cervantite was found in outcrop 7 in association with getchellite, stibnite and chalcostibite (Table 1). Its yellowish crystals (orthorhombic, class *mm2*) up to 2 mm long which have a grayish tint, were of platy and slatted habits and formed a radial beam (Text-fig. 17). Its XRD data were compared with those of the specimen from the mine in Oberwolfach, Freiburg region, Baden-Württemberg, Germany (Table 2). The chemical composition of the Izera Mts. specimen (Table 6) was determined for the plates (for representative analysis see item 01) and slats (item 02). The platy crystals had lower Sb amounts (74.02 wt. %, 1.86 apfu) than the slatted ones (77.03 wt. %, 1.94 apfu) and of course higher admixtures (e.g. As 1.52 wt. %, 0.06 apfu vs. 0.42 wt. %, 0.02 apfu, Bi 1.70 wt. %, 0.02 apfu vs. 0.61 wt. %, 0.01 apfu or Ge 0.17 wt. %, 0.007 apfu vs. 0.07 wt.

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* Possibly a misprint for Spiesglanzocker or Spiesglasocher (cf. Hoffmann 1817, pp. 124–125).

Mineral and location	No.	Sb	As	Bi	Pb	Ag	Fe	Mn	Sn	Ge	S	Se	O	Σ, wt. %
Cervantite														
Outcrop 7	01	74.018	1.516	1.705	1.284				0.426	0.166			20.883	99.998
	02	77.030	0.415	0.613	0.540		0.219		0.232	0.071			20.870	99.990
Kermesite														
Outcrop 8	03	73.071	0.533	0.906			0.138		0.365		19.663	0.364	4.952	99.991
Outcrop 9	04	74.585	0.186				0.140		0.147		19.774	0.196	4.961	99.989
	05	74.698	0.165				0.211				19.821	0.123	4.963	99.981
Schafarzikite														
Outcrop 7	06	66.657		0.230		0.176	15.026	0.211	0.079*				17.606	99.995

Crystallochemical formulae (apfu) calculated for oxygen atom amounts in the theoretical proportions.

01: $(Sb_{1.863}As_{0.062}Bi_{0.025}Pb_{0.019}Sn_{0.011}Ge_{0.007})_{\Sigma 1.987}O_{4.000}$

02: $(Sb_{1.940}As_{0.017}Fe_{0.012}Bi_{0.009}Pb_{0.008}Sn_{0.006}Ge_{0.003})_{\Sigma 1.999}O_{4.000}$

03: $(Sb_{1.939}As_{0.023}Bi_{0.014}Sn_{0.010}Fe_{0.008})_{\Sigma 1.994}(S_{1.981}Se_{0.015})_{\Sigma 1.996}O$

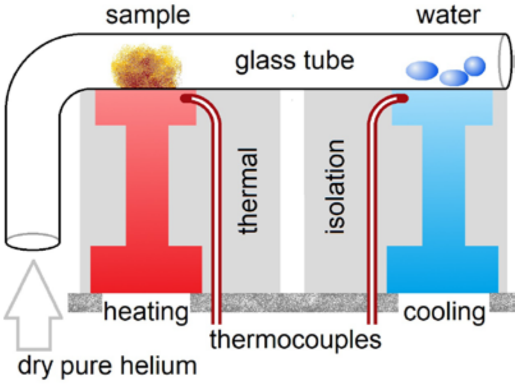
04: $(Sb_{1.976}As_{0.008}Fe_{0.008}Sn_{0.004})_{\Sigma 1.996}(S_{1.985}Se_{0.008})_{\Sigma 1.997}O$

05: $(Sb_{1.979}As_{0.007}Fe_{0.012})_{\Sigma 1.998}(S_{1.993}Se_{0.005})_{\Sigma 1.998}O$

06: $(Fe_{0.978}Mn_{0.014}Co_{0.005})_{\Sigma 0.997}(Sb_{1.990}Ag_{0.006}Bi_{0.004})_{\Sigma 2.000}O_{4.000}$

Table 6. Chemical composition of oxygenic antimony minerals, representative analyses; empty cells – component below detection limit (<~0.001 wt. %). * Co.

%, 0.003 apfu). The presumable presence of OH^- (as water) was also checked after sample grinding in a microscope crushing stage. The samples were dried from any possibly adsorbed water at a temperature of 40°C, then heated at 90°C and next at 110°C in the device shown in Text-fig. 18 (for the description see figure caption). Water was not detected; the same test for the sample from Oberwolfach gave also a negative result, confirmed by the IR spectrum. Moreover, the presence of even H_2O traces in the investigated cervantite samples was excluded by its heating followed by an attempt to get an evaporation product reaction with solid potassium lead iodide, a white compound that would instantly decompose even due to H_2O traces with appearance of the yellow PbI_2 (Biltz and Biltz 1928). Next the samples from Izera Mts. and from Oberwolfach were subjected to the influence of water vapour in closed ampoules at 60°C for 240 days; afterwards the presence of the OH^- groups was found by the IR spectrum and in the microscope device. The dried residues were checked by the XRD method – they were mixtures of substances which could not be clearly identified (this experiment was made by A.K. in the University of Tübingen). Hence it is likely that cervantite may be altered to other minerals or their mixtures ("ochres") both by epithermal and by hypergenic factors.



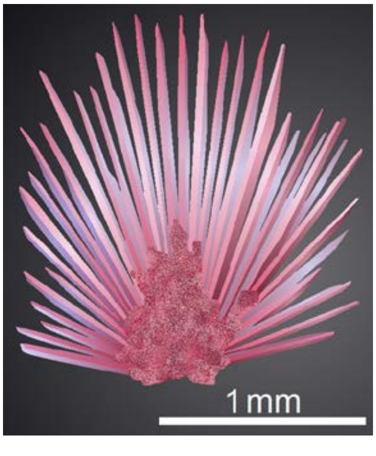
Text-fig. 18. Scheme of the device for determining the presence of water in a small amount of mineral, vertical section. The tube from silica glass has inner diameter c. 2 mm and length of the horizontal part c. 4 cm, heating is electric, cooling by water ice or solid carbon dioxide in a tiny container in the lower part of the device, the heating and cooling parts should be made of copper, helium should be perfectly dried, its flow must be very slow with the possibility of stopping. Only high quality thermo-insulating substance may be used. The device is to be placed on the microscope or binocular stage and the observation of appearing water droplets (or ice crystals) should be made in reflected light. The device and its use have been developed by AK on the basis of the Bolland's (1923, pp. 225–226) proposal of the determination of traces of water.

Kermesite Sb_2S_2O

This mineral for many centuries was a well recognizable component of the Sb ores due to its red colour and frequent acicular habit. Many names have been created for it, e.g. *Antimonblende, Goldschwefel, Purpurblende, Pyrantimonit, Pyrostibin, Pyrostibit* from Greek πυρο-(pyro i.e. fire)*, Rotantimon, rotes Federspießglas, rotes Spiesglaserz, Rotspiegelglanz(-erz), Rotspießglas(-erz)*, see e.g. Haditsch and Maus (1974). Hebenstreit (1737) in his presentation of the Sb-bearing substances as medicines characterized also this mineral and indicated mines at Freiberg, Germany, as its typical location of occurrence; he used the Latin names *antimonium rubrum* and synonymous *stibium rubrum* i.e. red antimony. The description of the Sb-S minerals in Cronstedt's book (1760, pp. 215–216) partly most probably refers to kermesite, especially these named *antimonium sulphure mineralisatum* (antimony mineralized by sulphur), *antimonium particulis sic dictum* (so called granular antimony), *rothes Spiesglaſerz, antimonium ſolare*. Most probably kermesite was also mentioned by Born (1772 p. 137) from Újbánya, Hungary (presently Nová Baňa, Slovakia) as *antimonium mineraliſatum cryſtalliſatum* which formed encrustations "blushing" quartz crystals. Coloured drawings of *red blend* (i.e. kermesite) from the Huel Boys mine, Cornwall, were published by Rashleigh (1797 plate XIX drawings *d* in figs. 1 and 2). The chemical composition of *faserige Roth-Spieſglanzerz* was studied by Klaproth (1802, pp. 178–182), who used the appellation *natürlicher Mineral-Kermes* ("κερμες" in Greek means "crimson", from "qurmizq" in Persian, also cf. "al-qirmiz" in Arabic and "qırmızı" in Azerbaijani language). Afterwards the name *kermès minéral* was used by Beudant (1824, p. 809) for "oxi-sulfure de l'antimoine"; he later applied *kermès* as the main name of this mineral, but he added synonyms *antimoine rouge*, *antimoine oxidé sulfuré*, *soufre doré*, *antimonblende* and *roth Spiesglanzerz* (Beudant 1832, p. 617). Chapman (1843, p. 61) used the name *kermesite* and *tinder ore*, a translation of *Zündererz*. However Nicol (1849, p. 485) wrote that analysis of the specimen of Zündererz from St. Andreasberg in Harz, Germany, has shown a chemical composition which suggested a mixture of fine-grained plumosite, arsenopyrite and pyrargyrite.

The Neue Hoffnung Gottes mine at Bräunsdorf near Freiberg in Saxony, Germany, was accepted as the type locality of kermesite (Gruner 1970). Finds of kermesite were not frequent; Shannon (1918b) mentioned it in two occurrences of the Sb ores in USA: Stanley mine in the Coeur d'Alene district, Idaho and Mojave mine, Kern county, California. An interesting locality Globe and Phoenix mine in Kwekwe district, Zimbabwe, with beautiful specimens of kermesite was described by Cairncross (2020). However, more frequent in the literature are short mentions of this mineral as from the Pezinok-Trojárová deposit in Slovakia (Chovan *et al.* 2002b), from polymetallic Sb-bearing sulphide ores at Rockliden, Västernorrland county, Sweden (Minz 2013) or from sulphide-carbonate veins with Sb minerals in Goesdorf, Luxembourg (Philippo and Hanson 2007). The total number of the kermesite occurrences is about 240, but very probably in a part of them the identification of this mineral was only tentative. In Poland it has not been found untill now; for a suggestion of its presence in pegmatite at Szklarska Poręba in the Karkonosze pluton (Mochnacka and Banaś 2000 p. 141) see footnote of the occurrences list in Appendix 1.

During the current investigations of the area of the authors' interest kermesite was found in its western part in outcrops 8 and 9. The following Sb minerals were in association with kermesite: boulangerite, berthierite, falkmanite and robinsonite in outcrop 8 and stibnite and boulangerite in outcrop 9 (Table 1). The specimen from outcrop 8 consisted of euhedral up to 2 mm long crystals (triclinic, class $\overline{1}$) of thin lath habits which formed a radial aggregate. On the merged, earliest part of the aggregate a silty clump of kermesite precipitated (Text-fig. 19). Kermesite from outcrop 9 formed by alteration of stibnite as accumulations of the grains up to 0.1 mm in size. Specimens from both outcrops were pink with various intensity of this colour. The chemical composition of kermesite from outcrop 8 is stable, practically the same both along the single crystal and of all the crystals. The representative analysis (Table 5 item 03) shows a commanding presence of admixtures: As c. 0.5 wt. %, 0.06 apfu, Bi c. 0.9 wt. %, 0.014 apfu, Fe c. 0.14 wt. %, 0.008 apfu, Sn c. 0.4 wt. %, 0.01 apfu and Se c. 0.04 wt. %, 0.015 apfu. Also the aggregate of fine-grained kermesite from this specimen had the same chemical composition. The presence of water or OH^- groups was checked (for the method see above in the cervantite description) but with negative result. The stability of chemical composition suggests no changes in the chemical features of the parent fluid of the mineral, and the different habits may be ex-



Text-fig. 19*. Kermesite, radial aggregate of fine crystals of lath habit with agglomeration of dusty grains of this mineral at the initial place of the laths crystallization, outcrop 8.

plained by temperature gradient. Differences in contents of admixtures were found in kermesite formed by mutation of stibnite in outcrop 9 (Table 6 items 04 and 05). These analyses were selected to show the range of the changes: As c. 0.16–0.19 wt. %, 0.007–0.008 apfu, Fe c. 0.14–0.21 wt. %, 0.008–0.012 apfu, Sn <~0.001–c. 0.15 wt. % , 0.000–0.004 apfu, Se c. 0.12–0.20 wt., 0.005–0.008 apfu. This may suggest changes of the chemical conditions of the reaction stibnite → kermesite.

The XRD data of the kermesite samples were obtained for 5 preparations – 3 from outcrop 8 (2 for euhedral crystals, 1 for dusty agglomeration) and 2 from outcrop 9 for the fine-grained product of the alteration of stibnite; no differences of any meaning were found, thus one representative pattern was presented (Table 2).

Schafarzikite $FeSb_2O_4$

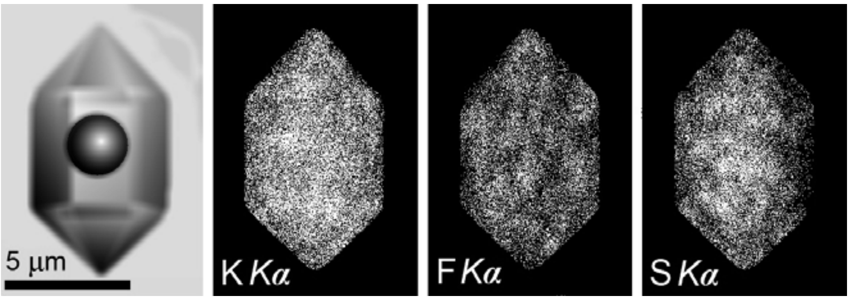
A new mineral found by Krenner (1921) at Pernek (Malé Karpaty Mts., formerly Hungary, now Slovak Republic) and he named it schafarzikite in honour of Prof. Franz (Ferenc) Schafarzik, geologist and mineralogist of the Polytechnic of Budapest. Krenner mentioned valentinite, sénarmontite and kermesite as the main Sb oxyminerals co-occurring with schafarzikite in the hypergenic alteration zone of this mine. A good description of the type locality with its mineralogical characteristic including schafarzikite was published by Sejkora *et al.* (2007). Polysomatic relations of this minerals with versiliaite and apuanite were the basis of the determination of the schafarzikite series (Mellini and Merlino 1979, Ferraris *et al.* 1986). Schafarzikite seems to occur rarely (or is rarely identified) in the ore deposits – probably only c. 15 locations all over the Earth. For example Dill *et al.* (1995) mentioned it in their publication on the antimony-gold vein from the Karma deposit in Cordillera Oriental, Bolivia. A very short note on its presence in the Drew Hill sulphide veins near Linneus, Maine, may be found in the book on minerals of this state (King and Foord 1994 p. 313). This mineral was also briefly described with two SEM and BSE images from the Sb mineral assemblage in Goesdorf (Philippo and Hatert 2018). Schafarzikite in Poland has been found so far only in the nonsulphide Zn-Pb ores in two mines Olkusz and Bolesław of the Silesia-Cracow region (Coppola et al, 2009); these ores formed from the deeper occurring sulphide Zn-Pb mineralization due the activity of meteoric water.

Text-fig. 20*. Schafarzikite, euhedral crystal probably with local twinning, outcrop 7.

In the currently studied Sb mineralization in the Karkonosze granitoid schafarzikite was recognized in outcrop 7 in the association with other Sb minerals, namely getchellite, stibnite, chalcostibite and cervantite (Table 1). Its identification by the XRD method was a result of comparison with the pattern of the synthetic $FeSb_2O_4$ compound (Table 2). The sample consisted of a few euhedral (Text-fig. 20) or subhedral crystals (tetragonal class *4/mmm*) up to 2.4 mm long, probably with local twinning, as suggested by the {100} prism faces. The admixtures in the chemical composition (Table 6 item 06, the average of 4 analyses with minimal differences) consisted of four components: Mn 0.211 wt. %, 0.014 apfu, Co 0.079 wt. %, 0.005 apfu, Ag 0.176 wt. %, 0.006 apfu and Bi 0.230 wt. %, 0.004 apfu. The analysis could be recalculated to practically theoretical formula and the nonstoichiometric formulae revealed by some analyses and discussed by Mellini *et al.* (1981) do not concern this case. Also the minor and unstable presence of fluoride ions in the defective structure (see e.g. Nowroozi *et al.* 2018) does not refer to the studied specimens, because the F presence was checked but not found.

Fluid inclusions

Three groups of quartz from the veins with Sb minerals were distinguished: a) crystals formed earlier than the Sb minerals, b) crystals in close paragenesis with Sb minerals and c) crystals formed later than the Sb minerals. In group a exact studies and measurements of 189 inclusions were made, in group b – 197 inclusions and in group c – 192 inclusions (total 578 inclusions). For these studies the inclusions 4–17 µm in size in separate positions in the host quartz were used to avoid or rather to minimize the



Text-fig. 21. Fluid inclusion (Th 129 ºC) in quartz paragenetic with native antimony from outcrop 1 and potassium, fluorine and sulfur *Kα* X-ray scan pictures of this inclusion heavily frozen and opened by microscope crushing stage.

possibility of the use of inclusions that were refilled, formed by dividing the parent inclusions into parts by recrystallization or migration (cf. Kozłowski and Matyszczak 2022a, pp. 17–18). The inclusions for measurements were selected from c. 1500 inclusions of the three groups which were thoroughly viewed. In all these inclusions only fillings have been found that formed by trapping of a one-phase (homogeneous) liquid water solution, as it was determined on the basis of homogenization or evaluation of phase proportions. Mostly the fillings at room temperature were two-phase (liquid and gas bubble), only in some inclusions a very thin rim of liquid CO_2 around the bubble was visible at c. 20°C, but in a certain number of cases it has been recognized only during cooling or freezing of the preparation. Jointly this component was observed in 35 inclusions from among all the 578 ones. Always the inclusion filling homogenized in liquid phase.

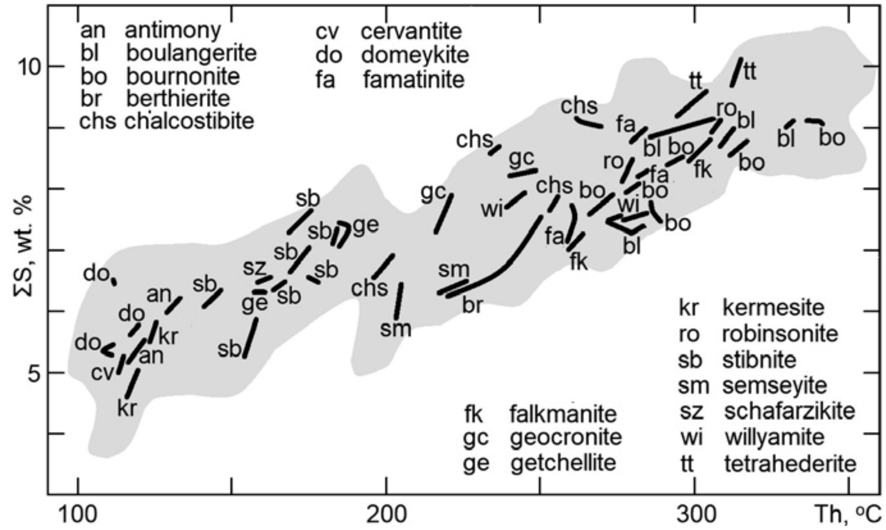
Inclusions in the pre-ore quartz (group a) homogenized in the temperature range 117–356°C, inclusions in the quartz paragenetic with the Sb minerals (group b) in the range 108–341°C and inclusions in the post-ore quartz (group c) from 98 to 327°C. The temperature ranges overlap because they concern 18 minerals in 10 outcrops. The total concentration of parent solutions and individual contents of the dissolved chemical components changed as well. The ranges are as follows (low vs. high temperature, in wt. %): inclusions in quartz of the group a – total salinity ΣS 4.8–10.5, Na_2CO_3 3.5–9.6, $Ca(HCO_3)_2$ 0.4–1.4, NaCl 0.05–0.23, KCl 0.02–0.12; group b – ΣS 4.6–10.1, Na_2CO_3 3.1–9.2, $Ca(HCO_3)_2$ 0.6–1.7, NaCl 0.04–0.19, KCl 0.02–0.09; group c – ΣS 3.8–9.2, Na_2CO_3 2.3–8.2, $Ca(HCO_3)_2$ 0.6–1.7, NaCl 0.04–0.12, KCl 0.02–0.09. Even in this scheme it is clear that the temperature decrease from group a to c is associated with some reduction in total salinity and in concentrations of Na_2CO_3 and NaCl and with a minor increase of the $Ca(HCO_3)_2$ concentration. The Th and concentration data for inclusions in quartz with Sb minerals in individual outcrops are presented in Table 7 and for the quartz paragenetic with each of the Sb minerals in Table 8. Inclusion fluids contained also some elements in very low concentrations. These elements were identified by X-ray scan pictures of the precipitate formed by drying of the fluid in the inclusion opened by the microscope crushing stage or of the preparation made by opening of the heavily frozen inclusion (Text-fig. 21). In this way 50 inclusions were

Outcrop, no.	Th, °C	ΣS, wt. %	Na_2CO_3, wt. %	$Ca(HCO_3)_2$, wt. %	NaCl, wt. %	KCl, wt. %
1	117–283	5.7–7.6	4.7–6.7	0.7–1.3	0.04–0.09	0.02–0.07
2	154–317	5.3–8.8	3.9–7.7	0.6–1.4	0.08–0.19	0.02–0.08
3	132–302	6.0–9.6	5.1–8.8	0.6–1.1	0.06–0.13	0.02–0.09
4	117–314	5.2–10.1	3.8–9.2	0.7–1.4	0.06–0.16	0.02–0.09
5	182–312	6.3–9.0	4.8–8.1	0.7–1.7	0.06–0.12	0.03–0.07
6	108–296	5.3–8.5	3.9–7.5	0.8–1.3	0.05–0.09	0.02–0.06
7	113–238	5.0–8.8	3.5–7.6	0.8–1.6	0.05–0.13	0.02–0.09
8	124–307	5.5–9.1	4.3–8.0	0.7–1.2	0.05–0.13	0.05–0.08
9	116–332	4.6–9.1	3.1–8.4	0.5–1.4	0.05–0.11	0.02–0.08
10	265–341	7.5–9.2	6.4–8.2	0.7–1.2	0.09–0.15	0.06–0.09

Table 7. Fluid inclusion data in quartz paragenetic with Sb minerals in individual outcrops; Th – homogenization temperature, ΣS – total salt concentration in inclusion fluid.

Sb mineral	Th, °C	ΣS, wt. %	Na_2CO_3, wt. %	$Ca(HCO_3)_2$, wt. %	NaCl, wt. %	KCl, wt. %
Antimony	117–133	5.2–6.3	3.8–5.3	0.8–1.4	0.06–0.08	0.02–0.03
Domeykite*	108–133	5.3–6.5	3.9–5.4	0.9–1.3	0.05–0.07	0.02–0.03
Getchellite	158–188	6,2–7.4	5.2–6.1	0.8–1.3	0.08–0.09	0.04–0.06
Stibnite	140–185	5.3–7.6	3.9–6.6	0.7–1.7	0.04–0.19	0.02–0.07
Willyamite	239–280	7.5–7.9	6.4–6.7	0.8–1.0	0.10–0.14	0.05–0.07
Berthierite	220–250	6.7–7.6	5.8–6.6	0.6–0.8	0.08–0.10	0.05–0.06
Boulangerite	280–332	7.3–9.1	6.3–8.4	0.5–1.0	0.07–0.10	0.04–0.08
Bournonite	272–341	7.4–9.3	6.4–8.2	0.7–1.0	0.08–0.15	0.05-0.09
Chalcostibite	196–268	6.6–9.1	5.6–7.8	0.8–1.2	0.06–0.13	0.03–0.09
Falkmanite	260–300	7.0–8.7	5.9–7.3	0.8–1.2	0.08–0.09	0.06–0.07
Famatinite	258–285	7.1–9.0	5.7–7.8	0.8–1.2	0.08–0.13	0.05–0.08
Geocronite	216–240	7.6–8.4	6.1–6.7	1.2–1.4	0.08–0.16	0.04–0.08
Robinsonite	274–307	7.4–9.7	6.1–8.0	0.7–1.4	0.08–0.13	0.04–0.09
Semseyite	203–226	5.9–6.5	4.8–5.4	0.8–1.5	0.06–0.08	0.03–0.04
Tetrahedrite	294–314	9.2–10.1	8.3–9.2	0.6–0.8	0.11–0.15	0.07–0.09
Cervantite	113–115	5.0–5.2	3.5–3.6	1.3–1.6	0.05–0.06	~0.02
Kermesite	116–126	4.6–5.8	3.1–4.8	0.9–1.4	0.05–0.07	~0.02
Schafarzikite	157–162	6.5–6.6	5.2–5.3	1.1–1.2	0.08–0.10	0.04–0.05

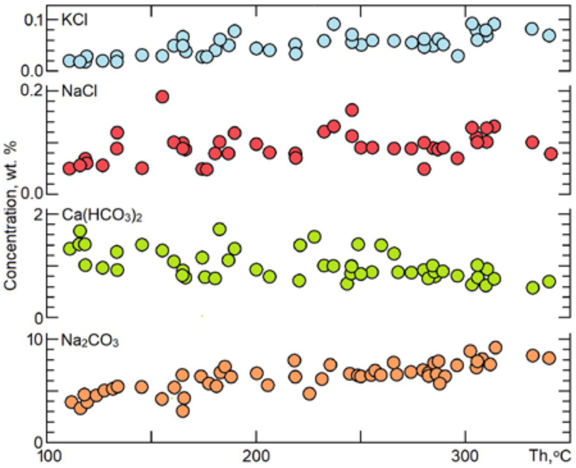
Table 8. Fluid inclusion data in quartz paragenetic individually with the Sb minerals; Th – homogenization temperature, ΣS – total salt concentration in inclusion fluid. * the Sb-bearing variety.



Text-fig. 22. Homogenization temperature (Th) vs total salinity (ΣS) of fluid inclusions in quartz group ***b*** paragenetic with the studied Sb minerals (black lines); gray area indicates extension of the same data for fluid inclusions in quartz groups a and c without the Sb minerals but surrounding the parageneses with them. Note: domeykite is the Sb-bearing variety.

verified and the presence of the following minor elements was confirmed (in parentheses number of the positive results): sulphur (47), iron (40), fluorine (24), magnesium (4) and aluminum (3). Also such a method was used to help in the determination of potassium (Text-fig. 21) and chlorine, confirming the data to calculate the KCl and NaCl contents in inclusion fluids.

The ΣS versus Th parameters of the crystallization of quartz are arranged in the diagram in an inclined zone from high to low values (Text-fig. 22). The gray field shows positions of the ΣS vs. Th points for all 381 inclusions in quartz of groups a and c. Black thick lines pass through the ΣS vs. Th points for 197 inclusions in quartz of group b closely paragenetic with the Sb minerals in 48 places of their occurrence in veins or nests. The extension of the two parameters of group b is different for various places, but mostly rather small and generally the direction of



Text-fig. 23. Concentration of the main chemical compounds dissolved in inclusion fluids vs. homogenization temperature of the appropriate inclusions, the data for quartz group ***b*** paragenetic with Sb minerals.

the changes follows cooling and dilution of the parent solutions of the host quartz.

The concentration of the chemical components of the parent fluids of quartz changed as well. A good example may be seen in the data from inclusions in quartz of group b (Text-fig. 23). The percentage of Na_2CO_3 gradually decreases from c. 8–10 wt. at c. 350°C to c. 3–4 wt. % at c. 100°C. But the percentage of $Ca(HCO_3)_2$ increases in the same temperature range from c. 0.7–0.8 to c. 1.7 wt. %. The points for NaCl are more scattered (c. 0.05–0.19 wt. %), but for KCl the decrease from c. 0.1 to c. 0.02 wt. % is quite consequent.

DISCUSSION

The investigated Sb minerals occurred in very local post-magmatic quartz veinlets or nests. They were small and traces of fluid migration from an external distant source (in any sense) were not found. Thus the process of formation of each of them and their parageneses was limited to a small space although it repeated at different places in a similar way. However, while cooling of the pluton rocks, solutions released from magma were present in the intergranular leaks as a chemically active factor and caused changes of the chemical composition of minerals, e.g. albitization of plagioclases (Nowakowski 1976, Nowakowski and Kozłowski 1981). There is also a possibility that the elements dispersed in the granitoid have been launched and after migration formed new minerals. The presence of antimony as a trace element in the Karkonosze granite has been stated by Gajda (1960). It was also checked by the authors and the detected contents in the studied area were as follows: in porphyritic granite, outcrop 1 – 0.39 pp, outcrop 4 – 0.35 ppm, outcrop 6 – 0.35 ppm, outcrop 7 – 0.37 ppm, outcrop 8 – 0.32 ppm, outcrop 9 – 0.39 and outcrop 10 – 0.33 ppm, average 0.36 ppm.; in equigranular granite, outcrop 2 – 0.20 ppm, outcrop 3 – 0.18 ppm and outcrop 5 – 0.21 ppm, average 0.20 ppm. These data are consistent with most of the values published by Brunfeld and Steinnes (1968, 1969) for granite: 0.21, 0.28, 0.30, 0.52 ppm, though these authors found a much lower value (0.06 ppm). The differences of the Sb contents in the Karkonosze granitoid may be related with the mingling and (or) mixing of the acid and more basic components of the intruding magmas (cf. Słaby and Martin 2008), since Brunfeld and Steinnes (1968, 1969) and Steinnes (1972) found 0.58 and 2.39 ppm in basalt, 0.90 ppm in diorite and 1.39 ppm in peridotite. Similar Sb contents were determined in igneous rocks by Onishi and Sandell (1955) and Parker (1967).

Stibnite from outcrop 3 (Text-fig. 6) of total volume c. 3 mm^3 has mass c.14 mg, thus it contains c. 10 mg Sb. This quantity of Sb occurs in c. 19,000 cm^3 of the equigranular granite or in c. 11,000 cm^3 of the porphyritic granite i.e. for example in cubes of the edges 28 and 22 cm respectively. If the assumption were accepted that approximately only 10 % Sb from granite would migrate to the newly forming Sb minerals, for the case under consideration the granite delivering Sb would have volumes of cubes with edges 58 and 48 cm long. This is consistent with the local scope of the formation process of the Sb minerals and the relatively narrow granitoid zone along the forming fissure or around the void in granite would be the source of the ore-forming elements. Probably it would be reasonable to remember the Christy's (2015) proposal of "anomalous mineralogical diversity" of some elements; he included Sb to the group of 15 "anomalously diverse elements" (Christy 2015, p. 40) to explain its specific role in mineral formation. But in this study the authors tried to characterize the appearance of the Sb minerals on the basis of the physical-chemical conditions. It is worth noting that accumulation and migration of antimony has been recognized also e.g. in thermal waters of geyser fields (Landrum *et al.* 2009) or in saline hydrothermal fluids (Pokrovski *et al.* 2006). Also other components of the ore minerals in the investigated outcrops could be a part of the trace elements in granite and they migrated in fluids towards the decreasing pressure i.e. towards the opening fissures and cracks. These fractures in granite were formed at various temperatures when the batholith cooled, therefore the elements migrated and minerals crystallized in the individual voids in different temperature ranges. For all the studied outcrops the general range has become marked by Th 341–108°C, but for single outcrops the ranges were: 1) 166, 2) 163, 3) 170, 4) 197, 5) 130, 6) 188, 7) 125, 8) 183, 9) 216 and 10) 76°C; note: 1) to 10) – numbers of outcrops.

The mineral-forming solutions were liquid phases with Na_2CO_3 as the main dissolved component although its concentration became lower as the temperature decreased. The second of the main components, $Ca(HCO_3)_2$, had higher concentrations at lower temperature. It is very probable that calcium might have been partly sourced in the albitization of oligoclase and this process used Na up from the fluids (Nowakowski 1976, Nowakowski and Kozłowski 1981). Potassium was the third cation apart from Na and Ca, but the solutions were distinctly poorer in it. The carbonate anion was the main one and chloride was clearly subordinate. This is also typical of present-day thermal waters in the Karkonosze pluton (cf. e.g. Fistek and Fistek 2005), but the carbonate anion could have had the source in the intruding magma, e.g. from waters absorbed by melt during migration as well as in waters that penetrated the solidified pluton. However, the concentration of the separate CO_2 phase is low, because only a small number of inclusions with trace concentrations of this component were found. The possibility of the presence of chloride anion in former thermal waters is confirmed by several mineral water springs of the Na-Cl type recently diagnosed in the Czech part of the Karkonosze pluton near Albrechtice (Goliáš *et al.* 2014). The probable evaluation is that the present-day composition of mineral waters cannot be directly compared with the past hydrotherms but they may be a reasonable suggestion about their type. Fluorine was present in most of the analysed fluid inclusions; this element facilitating migration of many cations is common as a minor component of the post-magmatic fluids in the whole Karkonosze pluton (Kozłowski and Matyszczak 2022a). Sulphur also has been found in almost all inclusions – it became the main component of sulphides and sulphosalts.

The chemical compositions of the investigated Sb minerals are usually quite similar to the theoretical formulae. Most frequently Ag, As, Bi, Cu and Pb are the admixtures located in the cation sites, slightly less often or even rarely Co, Ge, Hg, Mn, Mo, Ni, Sn and Zn. Essentially the main admixture elements in the Sb minerals formed components of their parageneses (see Table 1); no Ag minerals are present in these parageneses, however they have been found in several outcrops in the Karkonosze pluton (Kozłowski and Matyszczak 2022b, 2023), Minerals of Sn and Mo occur in the Karkonosze granitoid at Szklarska Poręba Huta close to the studied outcrops (Karwowski *et al.* 1973; Kozłowski *et al.* 1975). Also minerals of Ge, Hg, Se and Te are present in this pluton (Kozłowski and Matyszczak 2022b); the last two elements replace sulphur in minor to moderate part in the studied Sb minerals. On the other hand antimony became a significant admixture in domeykite, thus this mineral has been treated as its Sb variety. Moreover, antimony is a quite frequent admixture of paragenetic ore minerals (see Appendices 2 and 3). Mineral parageneses mostly formed under stable conditions. Even berthierite, which is stable over extremely narrow intervals of fO_2 and fS (Williams-Jones and Normand 1997), did not show any alterations. Only in a few cases probable changes mostly in the chemical conditions have been recognized. The changes caused zoning of the crystals of willyamite (outcrop 3), domeykite, geocronite and tetrahedrite (outcrop 4) – in these two outcrops admixtures were included in the grains changed during crystallization. Moreover, in outcrop 4 chalcopyrite and bournonite altered into a mixture of substances difficult to identify and sulphur migrated inside the antimony grain, in outcrop 8 falkmanite and galena have been partly replaced by bournonite and in outcrop 6 galena along its cleavage planes has been replaced by semseyite. On the radial aggregate of kermesite (outcrop 8) there precipitated a fine-grained agglomeration of this mineral, presumably due to a change in physical conditions, e.g. maybe a sudden increase in the concentration of the precipitating elements or cooling. Transformation of stibnite into kermesite in outcrop 9 occurred on the grounds of a change in the chemical composition of the parent solution. The antimony oxyminerals (cervantite, kermesite and schafarzikite) crystallized at low temperature (Th c. 110–160°C) as components of the final stage of the ore-mineral formation in the investigated area, however, not as direct product of oxidation but rather from epithermal solutions with involved surface waters.

CONCLUSIONS

Because antimony has been used for several thousand years in metallurgy, ceramics, glass production, cosmetology and later also in medicine as well as in alchemy, its ore occurrences were being searched for all this time. In Lower Silesia at least 65 locations with the Sb minerals have been found. But frequently the Sb ore mining was only local, thus the name(s) of the ore or Sb-containing substances (minerals) did not become widely known among specialists. For this reason, currently identification of the minerals described in the past may be difficult and (or) problematic. Thus the information on the occurrence of some Sb minerals on the basis of old publications may be uncertain.

In this study 18 Sb minerals (antimony, Sb-rich domeykite, getchellite, stibnite, willyamite, berthierite, boulangerite, bournonite, chalcostibite, falkmanite, famatinite, geocronite, robinsonite, semseyite, tetrahedrite-(Fe), cervantite, kermesite and schafarzikite) were identified in ten newly found outcrops in the Karkonosze pluton from southern part of Izera Mts. The occurrence of eight of them was detected for the first time in Lower Silesia.

The chemical composition of the Sb minerals was usually close to the theoretical formulae with Ag, As, Bi, Cu and Pb as the relatively frequent admixtures; Co, Ge, Hg, Mn, Mo, Ni, Sn and Zn appeared less often and in smaller quantities. Antimony occurred as a quite significant addition in domeykite, thus this mineral was treated as its Sb variety. Low amounts of antimony have been found in some theoretically Sb-free ore minerals from the studied parageneses.

Variations in the chemical features of the minerals of the same kind usually were very small in one crystal or even in one outcrop. Only in few cases crystal zoning or post-crystallization alterations of minerals were found. Nevertheless distinct differences in the chemical composition of minerals of the same kind but from various outcrops were not rare. This suggests in one outcrop mostly stable crystallization conditions, but distinctly changing from place to place in the investigated area.

Fluid inclusions were investigated in quartz closely adhered to the antimony minerals. The inclusion solution was of the $NaCO_3$-$Ca(HCO_3)_2$-NaCl-KCl type with minor concentrations of fluoride and sulphide ions. The general temperature decrease during crystallization of the Sb minerals was characterized by the Th values interval from 341 to 108°C. The individual Sb minerals formed in their separate temperature ranges of the values 76 to 216°C. In the latest part of formation of some of the studied parageneses there may have been an inflow of surface waters and few antimony oxyminerals formed.

The studied parageneses with Sb minerals formed most probably from the appropriate trace elements flushed out from granite, which next migrated in the intergranular solutions towards local fissures and cracks as places of precipitation.

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Appendix 1

Locations of occurrence of the antimony minerals in Lower Silesia described before 2024, vide also Text-fig. 1; the Legnica-Głogów Cu deposits (Oszczepalski 2007) not included. The asterisk (*) marks monographs, the authors of which collected earlier published data. For locations no. 24 and 62 vide Text-fig. 1 in Kozłowski and Matyszczak (2022).

1. Bardo – stibnite (Fiedler 1863; Traube 1888*; Hoehne 1941; Woch 2015)
2. Boguszów – bournonite, freieslebenite, polybasite, pyrargyrite (Mederski *et al.* 2020), tetrahedrite group (Fiedler 1863; Traube 1888*; Berg 1913; Hoehne 1941; Mederski *et al.* 2020)
3. Boguszyn – stibnite (Lis and Sylwestrzak 1986*)
4. Brzeg Dolny – stibnite (Fiedler 1863)
5. Bystrzyca Górna – stibnite (Volkmann 1720; Traube 1888*; Hoehne 1941), bournonite, miargyrite, native antimony, plagionite, pyrargyrite, senandorite, stephanite, tetrahedrite group, zoubekite (Pršek *et al*. 2019)
6. Chełmiec – bournonite (Lis and Sylwestrzak 1986*), tetrahedrite group (Fiedler 1863; Traube 1888*; Hoehne 1941)
7. Chromiec – bournonite, tetrahedrite group (Hoehne 1941)
8. Ciechanowice – polybasite, stephanite (Siuda 2012), stibnite (Anonymous 1796; Fiedler 1863; Birnbaum 1891), tetrahedrite group (Fiedler 1863; Siuda 2012)
9. Czarnów – native antimony, berthierite (Hoehne 1941; Sachanbiński 2005*; Mochnacka *et al*. 2009, 2015), boulangerite, bournonite, pyrargyrite, tetrahedrite group (Mochnacka *et al*. 2015), stibnite (Zimnoch 1983; Sachanbiński 2005*; Mochnacka *et al*. 2015; Woch 2015)
10. Dębowina – bindheimite, boulangerite, bournonite, stibiconite (Nejbert *et al*. 2013), stibnite (Kaluza 1818; Meißner 1805; Mączka and Stysz 2008; Nejbert *et al*. 2013), tetrahedrite group (Nejbert *et al*. 2013)
11. Dziećmorowice – stephanite, tetrahedrite group (Fiedler 1863; Traube 1888*; Petrascheck 1933; Hoehne 1941)
12. Dzikowiec – tetrahedrite group (Traube 1888*; Hoehne 1941; Lis and Sylwestrzak 1986*)
13. Gierczyn – bournonite (Lis and Sylwestrzak 1986*), “antimonite-(Bi)” i.e. stibnite (Kucha and Mochnacka 1986), pyrargyrite, tetrahedrite group (Piestrzyński and Mochnacka 2003; Sachanbiński 2005*)
14. Grodziec – tetrahedrite group (Lis and Sylwestrzak 1986*)
15. Grudno – boulangerite, stibnite (Lis and Sylwestrzak 1986*), bournonite, pyrargyrite, tetrahedrite group (Paulo and Salamon 1972)
16. Iwiny – tetrahedrite group (Lis and Sylwestrzak 1986*)
17. Jabłów – boulangerite, bournonite (Traube 1888*; Hoehne 1941; Lis and Sylwestrzak 1986*), tetrahedrite group (Buch 1802; Fiedler 1863; Traube 1888*; Birnbaum 1891; Berg 1913; Hoehne 1941)
18. Janowice Wielkie – tetrahedrite group (Fiedler 1863)
19. Jedlinka – tetrahedrite group (Lis and Sylwestrzak 1986*)
20. Karpacz – stibnite (Hoehne 1941)
21. Klecza – tetrahedrite group (Paulo and Salamon 1973)
22. Kletno – aramayoite, tetrahedrite group (Lis and Sylwestrzak 1986*), miargyrite (Banaś and Mochnacka 1986)
23. Kowary – stibnite (Kretschmar 1662; Volkelt 1775), pyrargyrite, tetrahedrite group (Mochnacka and Banaś 2000; Sachanbiński 2005*; Mochnacka *et al*. 2015)
24. Krowia Kopa Mt. – pyrargyrite (Kozłowski and Matyszczak 2022)
25. Książ – stibnite (Lis and Sylwestrzak 1986*)
26. Leszczyna – tetrahedrite group (Hoehne 1941; Lis and Sylwestrzak 1986*)
27. Leszczyniec tetrahedrite group (Lis and Sylwestrzak 1986*)
28. Lipa – tetrahedrite group (Fiedler 1863; Hoehne 1941)
29. Markocice – tetrahedrite group (Mochnacka *et al*. 2015)
30. Męcinka – tetrahedrite group (Traube 1888*; Neuhaus 1936; Lis and Sylwestrzak 1986*)
31. Michałowice – owyheeite (Kozłowski and Matyszczak 2022), tetrahedrite group (Gajda 1960; Karwowski *et al*. 1983; Kozłowski and Matyszczak 2018)
32. Miedzianka – boulangerite, famatinite (Lis and Sylwestrzak 1986*), geocronite (Hoehne 1953; Sachanbiński 2005*), pyrargyrite, stibnite (Raumer 1813; Websky 1866; Traube 1888*; Schneider 1894; Sachanbiński 2005*; Mochnacka *et al*. 2012), polybasite, stephanite (Websky 1866; Traube 1888*; Hoehne 1941; Sachanbiński 2005*; Mochnacka *et al*. 2012), “stibioenargite” (Mochnacka *et al*. 2012), tetrahedrite group (Raumer 1813; Fiedler 1863; Traube 1888*; Schneider 1894; Birnbaum 1891; Hoehne 1941; Mochnacka *et al*. 2012)
33. Mniszków – stibnite (Volkelt 1775)
34. Modliszów – stibnite (Kapf 1794; Hoehne 1941), tetrahedrite group (Hoehne 1941; Lis and Sylwestrzak 1986*)
35. Niedźwiedzice – tetrahedrite group (Lis and Sylwestrzak 1986*)
36. Nielestno – stibnite (Volkmann 1720)
37. Nowa Ruda – stibnite (Lis and Sylwestrzak 1986*)
38. Nowa Wieś Kłodzka – tetrahedrite group (Kaluza 1818; Fiedler 1863)
39. Piaskowa Mt. – tsnigriite (Kozłowski and Matyszczak 2022)
40. Pilchowice – tetrahedrite group (Paulo and Salamon 1973)
41. Podgórzyn – stibnite (Volkmann 1720; Weigel 1800, Meißner 1805)
42. Przecznica – pyrargyrite, tetrahedrite group (Piestrzyński and Mochnacka 2003)
43. Radomice – tetrahedrite group (Paulo and Salamon 1973)
44. Radzimowice – boulangerite, bournonite (Schirm 1887; Traube 1888*; Hoehne 1941; Mikulski 2005; Paulo and Salamon 1974), jamesonite (Mikulski 2005; Paulo and Salamon 1974), stibnite (Fiedler 1863; Schirm 1887; Paulo

and Salamon 1974; Mikulski 2005; Parafiniuk and Siuda 2006), tetrahedrite group (Fiedler 1863; Traube 1888*; Birnbaum 1891; Hoehne 1941; Paulo and Salamon 1974; Siuda 2001; Mikulski 2005)

45. Rędziny – bournonite (Sachanbiński 2005*), giessenite, kobellite, (Gołębiowska *et al.* 2006, 2012), izoklakeite (Mochnacka *et al*. 2015), tetrahedrite group (Gołębiowska *et al.* 2006, 2012; Mochnacka *et al*. 2015)
46. Siodlasta Mt. – tetrahedrite group (Beyschlag and Krusch 1913)
47. Smolarnia Dolna – stibnite (Volkmann 1720)
48. Sobięcin – tetrahedrite group (Traube 1888*; Hoehne 1941, Lis and Sylwestrzak 1986*)
49. Srebrna Góra – tetrahedrite group (Traube 1888*; Hoehne 1941; Lis and Sylwestrzak 1986*)
50. Stanisławów – tetrahedrite group (Karwowski and Kowalski 1981)
51. Stara Kamienica schist belt – costibite (Piestrzyński and Mochnacka 2003; Sachanbiński 2005*) "antimonite-(Bi)" i.e. stibnite, boulangerite, bournonite, pyrargyrite, stephanite, tetrahedrite group (Mochnacka *et al*. 2015), stibnite (Woch 2015), willyamite (Piestrzela 2019)
52. Stary Julianów – stephanite, tetrahedrite group (Petrascheck 1933)
53. Sucha Mt, – tetrahedrite group (Kozłowski and Matyszczak 2023)
54. Szklarska Poręba** – tetrahedrite group (Pieczka and Gołębiowska 2002)
55. Szklary – native antimony (Pieczka *et al*. 2015), paradocrasite, stibarsen (Pieczka 2000), stibioniobite = stibiocolumbite? (Pieczka *et al*. 1997)
56. Tylice, Winna Mt. – tetrahedrite group (Traube 1888*)
57. Wałbrzych – tetrahedrite group (Lis and Sylwestrzak 1986*)
58. Wielki Staw – stibnite (Volkmann 1720)
59. Wieściszowice – boulangerite, bournonite, jamesonite (Sachanbiński 2005*; Mochnacka *et al.* 2015), tetrahedrite group (Traube 1888*; Hoehne 1941, Mochnacka *et al*. 2015)
60. Wilków – tetrahedrite group (Lis and Sylwestrzak 1986*)
61. Wojcieszów – boulangerite, bournonite, jamesonite, stibnite, tetrahedrite group (Manecki 1965)
62. Wołek Mt. – freieslebenite (Kozłowski and Matyszczak 2022)
63. Zdrojowisko – ullmannite (Zakrzewski 1975)
64. Złotoryja – tetrahedrite group (Traube 1888*)
65. Złoty Stok – stibnite (Fiedler 1863; Traube 1888*; Petrascheck 1934; Hoehne 1941)

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** Mochnacka and Banaś (2000 p. 141, Table 1 item 1.3.1) included kermesite to the list of minerals from Szklarska Poręba as the citation from Gajda (1960), however this author did not write about this mineral. May be the citation is z misprint for kämmererite i.e. chromium-bearing clinochlore described by Gajda (1960, pp. 573–574).

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Appendix 2

Chemical composition of ore minerals associated with the investigated Sb minerals; empty cells – component below detection limit (<~0.001 wt. %). Note: 19 specimens contain Sb as minor admixture (0.205–5.708 wt. %) and 3 as trace (~0.001 wt. %).

Mineral and location	No.	Cu	Ag	Au	Pb	Fe	Mn	Zn	As	Sb	Bi	In	Ge	Co	Ni	Hg	Tl	Mo	W	S	Se	Te	Σ, wt. %
Aikinite																							
Outcrop 1	01	10.878			35.826	0.136					36.279					0.045	0.067			16.658	0.109		99.998
Outcrop 10	02	10.898	0.169		35.753	0.107				0.278	37.913				0.031					16.696	0.124	0.018	99.987
Bismuth, native																							
Outcrop 2	03	0.455	0.275	trace	1.798				0.802	5.708	90.953												99.981
Outcrop 4	04	0.186	trace		1.013			0.064	0.330	1.369	97.025												99.987
Arsenopyrite																							
Outcrop 3	05		0.197			33.019			45.023	0.889				0.323	0.357					19.407	0.240		99.996
Bismuthinite																							
Outcrop 3	06	0.112							0.132	0.262	80.688									18.704	0.091		99.989
Outcrop 4	07	0.164			0.973	0.164			trace	trace	79.584									18.802	0.132	0.094	99.992
Outcrop 5	08	0.292	9.128		0.368	0.410			trace	trace	79.609									18.998	0.173		99.978
Outcrop 6	09	0.113			0.695	0.154			0.219	0.504	79.369									18.849	0.093		99.996
Outcrop 9	10	0.352			0.861				0.522	1.039	78.294									18.t38	0.183		99.989
Outcrop 10	11				0.364				0.528	0.435	80.126									18.539			99,992
Bornite																							
Outcrop 1	12	61.161	0.148		2,553	10.774	0.129													24.964	9.262		99.991
Outcrop 2	13	59.623			1.986	9.903		0.790	1.336		2.085	0.169								23.974	0.121		99.988
Outcrop 5	14	59.240			3.643	10,331		0.285	1.203		1,198		0.083							23.995			99.978
Chalcocite																							
Outcrop 1	15	79.086				0.456	0.173													20.075	1.198		99.988
Outcrop 6	16	78.575				0.522		0.246					0.182							19.927	0.297	0.236	99.986
Chalcopyrite																							
Outcrop 1	17	33.319	0.466			29,617	0.504	0.672												24.047	1.362		99.987
Outcrop 3	18	32.836	0.978	trace		29.332		0.488				0.738								33.226	2.398		99.993
Outcrop 4	19	32.374	0.455	trace	1.637	28.593					0.991	0.605			0.587					33.097	1.704		99.989
Outcrop 5	20	32.241			1.834	28.498	0.341				1.523				0.274		0.632			32.636	2.017		99.996
Outcrop 6	21	32.692				29.296		0.631		1.370				0.253	0.314					33.766	1.184	0.479	99.985
Outcrop 7	22	33.182	1.329			29.341									0.503					33.643	1.310	0.684	99.992
Outcrop 10	23	31.286	1.415			28.169				2.364				0.433	0.678					32.550	2.153	0.938	99.981
Cosalite																							
Outcrop 9	24	0.092	0.065	trace	41.469					0.213	41.712					0.142				16.139	0.151		99.983
Emplectite																							
Outcrop 1	25	18.938				0.306	0.083		0.205	3.179	57.701									19.238	0.335		99.985
Galena																							
Outcrop 1	26	0.511	0.183		85.124						0.442									13.460	0.268		99.988
Outcrop 2	27	0.651			84.768	0.262					0.536									13.613	0.168		99.998
Outcrop 6	28	0.429			85.121				0.190	0.206	0.441									13.367	0.233		99.987
Outcrop 8	29	0.598			84.896	0.216				0.262										13.481	9.269	0.272	99.994
Outcrop 9	30	0.294			84.582					0.410	0.791									13.267	0.335	0.32	99.999
Outcrop 10	31	0.510			85.003					0.360										13.279	0.400	0.431	99.983
Galenobismutite																							
Outcrop 6	32	0.264			26.441		0.127		0.392	0.276	55.162					0.186				17.047			99.995
Molybdenite																							
Outcrop 2	33					0.209												59.129	0.571	39.892	0.197		99.998
Outcrop 4	34	0.159				0.175												59.436		40.077	0.148		99.995
Outcrop 6	35						0.165[a]											59.453	0.349	40.023			99.994
Outcrop 7	36	0.081				0.108												59.174	0.460	40.021	0.148		99.992
Pyrrhotite																							
Outcrop 2	37	0.243				58.005								0.227	0.669					40.854			99.998
Outcrop 5	38	0.310				60.213									0.358					39.114			99.995
Outcrop 8	39					60.040	0.132							0.140	0.211					38. 474			99.997
Outcrop 9	40	0.382				69.179	0.180	0.157							0.567					38.524			99.989
Pyrite																							
Outcrop 1	41	0.688	0.269			45.291		0.217	0.269											53.052			99.988
Outcrop 2	42	0.578				45.353		0.325									0.339			53.071	0.327		99.993
Outcrop 3	43	0.369				45.687			0.373	0.505										53.057			99,991
Outcrop 4	44	0.623	0.440		1.354	44.357														51.859	1.354		99.987
Outcrop 5	45	0.842	trace	0.488		45.231														52.902	0.523		99.986
Outcrop 6	46	0.840				45.202		0.216											0.378[b]	52.639	0.716		99.991
Outcrop 7	47	0.630				45.124								0.146	0.388					52.781	0.916		99.985
Outcrop 8	48	0.421				45.336			0.808	trace				0.243	0.341					52.839			99.988
Outcrop 9	49	trace			0.687	45.029								0.440	0.681					53.148			99.985
Outcrop 10	50	trace	0.442		1.190	44.164			0.922					0.483	0.578					52.220			99.999
Sphalerite																							
Outcrop 6	51		0.154			0.625	0.335	64.744	0.762	0.571[c]			0.089			0.408				32.308			99.996

[a] Nb, [b] V, [c] Cd; moreover magnetite in outcrop 5: Fe^{3+} 47.718, Fe^{2+} 23.954, Ti 0.432, Zn 0.170, V. 0.044, O 27.674, Σ 99.992 (wt. %).

Appendix 3

Crystallochemical formulae (apfu) of the ore minerals associated with the Sb ones; 01–52 numbers of the analyses in Appendix 2.

Aikinite
01. Outcrop 1 $(Pb_{0.996}Tl_{0.002}Hg_{0.001})_{\Sigma 0.999}(Cu_{0.986}Fe_{0.014})_{\Sigma 1.000}Bi_{1.000}(S_{2.992}Se_{0.008})_{\Sigma 3.000}$
02. Outcrop 10 $(Pb_{0.991}Ag_{0.009})_{\Sigma 1.000}(Cu_{0.985}Fe_{0.011}Ni_{0.})_{\Sigma 0.999}(Bi_{0/987}Sb_{0.013})_{\Sigma 1.000}(S_{2.990}Se_{0.009}Te_{0.001})_{\Sigma 3.000}$

Bismuth, native
03. Outcrop 2 $(Bi_{0.851}Sb_{0.092}As_{0.021}Pb_{0.017}Cu_{0.014}Ag_{0.005})_{\Sigma 1.000}$
04. Outcrop 4 $(Bi_{0.850}Sb_{0.023}Pb_{0.010}As_{0.009}Cu_{0.006}Zn_{0.002})_{\Sigma 1.000}$

Arsenopyrite
05. Outcrop 3 $(Fe_{0.972}Cu_{0.014}Ni_{0.010}Co_{0.009}Ag_{0.003})_{\Sigma 1.008}(As_{0.988}Sb_{0.012})_{\Sigma 1.000}(S_{0.995}Se_{0.005})_{\Sigma 1.000}$

Bismuthinite
06. Outcrop 3 $(Bi_{1.976}Sb_{0.011}Cu_{0.009})_{\Sigma 1.996}(S_{2.985}As_{0.009}Se_{0.006})_{\Sigma 3.000}$
07. Outcrop 4 $(Bi_{1.940}Pb_{0.0224}Cu_{0.019}Fe_{0.015})_{\Sigma 1.998}(S_{2.987}Se_{0.009}Te_{0.004})_{\Sigma 3.000}$
08. Outcrop 5 $(Bi_{1.922}Fe_{0.037}Cu_{0.023}Pb_{0.009}Ag_{0.006})_{\Sigma 1.997}(S_{2.989}Se_{0.011})_{\Sigma 3.000}$
09. Outcrop 6 $(Bi_{1.925}Sb_{0.021}Pb_{0.017}Fe_{0.014}Cu_{0.009})_{\Sigma 1.986}(S_{2.979}As_{0.015}Se_{0.006})_{\Sigma 3.000}$
10. Outcrop 9 $(Bi_{1.894}Sb_{0.043}Cu_{0.028}Pb_{0.021})_{\Sigma 1.986}(S_{2.954}As_{0.035}Se_{0.011})_{\Sigma 3.000}$
11. Outcrop 10 $(Bi_{1.967}Sb_{0.018}Pb_{0.009})_{\Sigma 1.994}(S_{2.964}As_{0.036})_{\Sigma 3.000}$

Bornite
12. Outcrop 1 $(Cu_{4.925}Pb_{0.063}Ag_{0.007})_{\Sigma 4.995}(Fe_{0.987}Mn_{0.012})_{\Sigma 0.999}(S_{3.983}Se_{0.017})_{\Sigma 4.000}$
13. Outcrop 2 $(Cu_{4.894}Bi_{0.052}Pb_{0.050})_{\Sigma 4.996}(Fe_{0.925}Zn_{0.063}In_{0.008})_{\Sigma 0.996}(S_{3.899}As_{0.093}Se_{0.008})_{\Sigma 4.000}$
14. Outcrop 5 $(Cu_{4.878}Pb_{0.092}Bi_{0.030})_{\Sigma 5.000}(Fe_{0.968}Zn_{0.023}Ge_{0.006})_{\Sigma 0.997}(S_{3.898}As_{0.102})_{\Sigma 4.000}$

Chalcocite
15. Outcrop 1 $(Cu_{1.980}Fe_{0.013}Mn_{0.005})_{\Sigma 1.998}(S_{0.996}Se_{0.004})_{\Sigma 1.000}$
16. Outcrop 6 $(Cu_{1.972}Fe_{0.015}Zn_{0.006}Ge_{0.004})_{\Sigma 1.997}(S_{0.991}Se_{0.006}Te_{0.003})_{\Sigma 1.000}$

Chalcopyrite
17. Outcrop 1 $(Cu_{0.972}Zn_{0.019}Ag_{0.008})_{\Sigma 0.999}(Fe_{0.983}Mn_{0.017})_{\Sigma 1.000}(S_{1.968}Se_{0.032})_{\Sigma 2.000}$
18. Outcrop 3 $(Cu_{0.969}Zn_{0.014}Ag_{0.017})_{\Sigma 1.000}(Fe_{0.985}In_{0.012})_{\Sigma 0.997}(S_{1.943}Se_{0.057})_{\Sigma 2.000}$
19. Outcrop 4 $(Cu_{0.967}Pb_{0.015}Bi_{0.009}Ag_{0.008})_{\Sigma 0.999}(Fe_{0.970}Ni_{0.019}In_{0.010})_{\Sigma 0.999}(S_{1.959}Se_{0.041})_{\Sigma 2.000}$
20. Outcrop 5 $(Cu_{0.973}Pb_{0.017}Bi_{0.014}Tl_{0.006})_{\Sigma 1.000}(Fe_{0.977}Mn_{0.012}Ni_{0.009})_{\Sigma 0.998}(S_{1.951}Se_{0.049})_{\Sigma 2.000}$
21. Outcrop 6 $(Cu_{0.960}Sb_{0.021}Zn_{0.018})_{\Sigma 0.999}(Fe_{0.979}Ni_{0.010}Co_{0.008})_{\Sigma 0.997}(S_{1.965}Se_{0.028}Te_{0.007})_{\Sigma 2.000}$
22. Outcrop 7 $(Cu_{0.975}Ag_{0.023})_{\Sigma 0.999}(Fe_{0.981}Ni_{0.016})_{\Sigma 0.997}(S_{1.959}Se_{0.031}Te_{0.010})_{\Sigma 2.000}$
23. Outcrop 10 $(Cu_{0.938}Sb_{0.037}Ag_{0.025})_{\Sigma 1.000}(Fe_{0.961}Ni_{0.022}Co_{0.014})_{\Sigma 0.997}(S_{1.934}Se_{0.052}Te_{0.014})_{\Sigma 2.000}$

Cosalite
24. Outcrop 9 $(Pb_{1.981}Cu_{0.014}Ag_{0.006})_{\Sigma 2.001}(Bi_{1.976}Sb_{0.017}Hg_{0.007})_{\Sigma 2.000}(S_{4.981}Se_{0.019})_{\Sigma 5.000}$

Emplectite
25. Outcrop 1 $(Cu_{0.982}Fe_{0.018}Mn_{0.005})_{\Sigma 0.995}(Bi_{0.910}Sb_{0.086})_{\Sigma 0.996}(S_{1.977}Se_{0.008}As_{0.009})_{\Sigma 2.000}$

Galena
26. Outcrop 1 $(Pb_{0.971}Cu_{0.019}Bi_{0.005}Ag_{0.004})_{\Sigma 0.999}(S_{0.992}Se_{0.008})_{\Sigma 1.000}$
27. Outcrop 2 $(Pb_{0.959}Cu_{0.024}Fe_{0.011}Bi_{0.006})_{\Sigma 1.000}(S_{0.995}Se_{0.005})_{\Sigma 1.000}$
28. Outcrop 6 $(Pb_{0.973}Cu_{0.016}Bi_{0.005}Sb_{0.004})_{\Sigma 0.998}(S_{0.987}Se_{0.007}As_{0.006})_{\Sigma 1.000}$
29. Outcrop 8 $(Pb_{0.962}Cu_{0.022}Fe_{0.009}Sb_{0.005})_{\Sigma 0.998}(S_{0.987}Se_{0.008}Te_{0.005})_{\Sigma 1.000}$
30. Outcrop 9 $(Pb_{0.971}Cu_{0.011}Bi_{0.009}Sb_{0.008})_{\Sigma 0.999}(S_{0.984}Se_{0.010}Te_{0.006})_{\Sigma 1.000}$
31. Outcrop 10 $(Pb_{0.971}Cu_{0.019}Sb_{0.007})_{\Sigma 0.997}(S_{0.980}Se_{0.012}Te_{0.008})_{\Sigma 1.000}$

Galenobismutite
32. Outcrop 6 $(Pb_{0.951}Cu_{0.031}Fe_{0.017})_{\Sigma 0.999}(Bi_{1.967}Sb_{0.022}Hg_{0.007})_{\Sigma 1.997}(S_{3.961}As_{0.039})_{\Sigma 4.000}$

Molybdenite
33. Outcrop 2 $(Mo_{0.989}Fe_{0.006}W_{0.005})_{\Sigma 1.000}(S_{1.996}Se_{0.004})_{\Sigma 2.000}$
34. Outcrop 4 $(Mo_{0.990}Fe_{0.005}Cu_{0.004})_{\Sigma 1.000}(S_{1.997}Se_{0.003})_{\Sigma 2.000}$
35. Outcrop 6 $(Mo_{0.993}Nb_{0.003}W_{0.003})_{\Sigma 0.999}S_{2.000}$
36. Outcrop 7 $(Mo_{0.987}W_{0.004}Fe_{0.003}Cu_{0.002})_{\Sigma 0.996}(S_{1.997}Se_{0.003})_{\Sigma 2.000}$

Pyrrhotite
37. Outcrop 2 $(Fe_{0.869}Ni_{0.009}Co_{0.003}Cu_{0.003})_{\Sigma 0.884}S_{1.000}$
38. Outcrop 5 $(Fe_{0.884}Ni_{0.005}Cu_{0.004})_{\Sigma 0.893}S_{1.000}$
39. Outcrop 8 $(Fe_{0.911}Ni_{0.003}Co_{0.002}Mn_{0.002})_{\Sigma 0.918}S_{1.000}$
40. Outcrop 9 $(Fe_{0.897}Ni_{0.008}Cu_{0.005}Mn_{0.003}Zn_{0.002})_{\Sigma 0.915}S_{1.000}$

Pyrite
41. Outcrop 1 $(Fe_{0.977}Cu_{0.013}Zn_{0.004}Ag_{0.003})_{\Sigma 0.997}(S_{1.992}As_{0.008})_{\Sigma 2.000}$
42. Outcrop 2 $(Fe_{0.979}Cu_{0.011}Zn_{0.006}Tl_{0.002})_{\Sigma 0.998}(S_{1.995}Se_{0.005})_{\Sigma 2.000}$
43. Outcrop 3 $(Fe_{0.986}Cu_{0.007}Sb_{0.005})_{\Sigma 0.998}(S_{1.994}As_{0.006})_{\Sigma 2.000}$
44. Outcrop 4 $(Fe_{0.972}Cu_{0.012}Pb_{0.008}Ag_{0.005})_{\Sigma 0.997}(S_{1.979}Se_{0.021})_{\Sigma 2.000}$
45. Outcrop 5 $(Fe_{0.978}Cu_{0.016}Au_{0.003})_{\Sigma 0.997}(S_{1.992}Se_{0.008})_{\Sigma 2.000}$
46. Outcrop 6 $(Fe_{0.980}Cu_{0.010}Zn_{0.004}V_{0.003})_{\Sigma 0.997}(S_{1.989}Se_{0.011})_{\Sigma 2.000}$
47. Outcrop 7 $(Fe_{0.975}Cu_{0.012}Ni_{0.008}Co_{0.003})_{\Sigma 0.998}(S_{1.986}Se_{0.014})_{\Sigma 2.000}$
48. Outcrop 8 $(Fe_{0.979}Cu_{0.008}Ni_{0.007}Co_{0.005})_{\Sigma 0.999}(S_{1.987}As_{0.013})_{\Sigma 2.000}$
49. Outcrop 9 $(Fe_{0.973}Ni_{0.014}Co_{0.009}Pb_{0.004})_{\Sigma 1.000}S_{2.000}$
50. Outcrop 10 $(Fe_{0.964}Ni_{0.012}Co_{0.010}Pb_{0.007}Ag_{0.005})_{\Sigma 0.998}(S_{1.985}As_{0.015})_{\Sigma 2.000}$

Sphalerite
51. Outcrop 6 $(Zn_{0.979}Fe_{0.011}Mn_{0.006}Cd_{0.005}Hg_{0.002}Ag_{0.001}Ge_{0.001})_{\Sigma 0.999}(S_{3.990}As_{0.010})_{\Sigma 1.000}$

Magnetite
52. Outcrop 5 $(Fe_{0.992}Zn_{0.006})_{\Sigma 0.998}(Fe_{1.976}Ti_{0.021}V_{0.002})_{\Sigma 1.999}O_{4.000}$