Geochemistry of tetrahedrite group minerals and associated silver paragenesis in the Boguszów baryte deposit, Poland

Sławomir MEDERSKI¹, *, Jaroslav PRŠEK¹ and Żaneta NIEMASZ¹

¹ AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Kraków, Poland


Associate Editor: Jacek Szczepański

Primary ore mineralization in the abandoned Boguszów baryte-polymetallic deposit, located in the Intra-Sudetic Depression, was studied by reflected light microscopy and electron microprobe. Ore minerals, occurring as veinlets, irregular aggregates and lenses in baryte veins are hosted by the Upper Carboniferous Chelmiec rhyodacite laccolith. They are dominated by galena, sphalerite (with Cd up to 0.04 apfu) and tetrahedrite group minerals (TGM). Four generations of the TGM were distinguished according to textural features and Ag content: (1) low-Ag tetrahedrite-(Zn) (Ag: 0.22–0.6 apfu), (2) Ag-enriched tetrahedrite-(Zn) and Ag-enriched tetrahedrite-(Fe) (Ag: 0.71–1.45 apfu), (3) members of the freibergite series: "freibergite-(Fe)" and "freibergite-(Zn)" (Ag: 3.21–3.48 apfu, Hg: up to 0.75 apfu), (4) member of the "freibergite-(Fe)" series (Ag: 5.32–5.78 apfu). Several elongated inclusions of Ag-bearing sulphosalts within galena crystals were observed (members of the series "freibergite-(Fe)" and "freibergite-(Zn)"; pyrargyrite and polybasite). These polymetallic silver-bearing ores were mined in Boguszów from the 15th to the 19th century. Additionally, small grains of cobalt-enriched löllingite and gersdorffite were observed, which were formed from fluids sourced from the ultramafic basement. The textural characteristics of the ore, the mineral paragenesis and the chemical composition of individual ore minerals indicate low-temperature crystallization conditions.

Key words: Boguszów, baryte veins, silver mineralization, tetrahedrite.

INTRODUCTION

Silver mineralization in the form of silver minerals, tetrahedrite group minerals (TGM) or in the form of admixtures in galena or bornite is common in different genetic types of base metal deposits. It occurs primarily in epithermal systems (e.g., Gemmell et al., 1989; Plumlee and Whitehouse-Veaux, 1994; Cheilletz et al., 2002; Sack and Goodell, 2002; Sack et al., 2003; Bestemianova and Grinev, 2017). In these systems, baryte is a major gangue mineral phase. The presence of silver mineralization is also recorded in other deposit types, including skarn, volcanogenic massive sulphide, sedimentary-exhalative and sediment-hosted type deposits (e.g., Grossou-Valta et al., 1990; Höller and Gandhi, 1995; Shalaby et al., 2004; Kołodziejczyk et al., 2016; Kozub-Budzyń and Piesztyński, 2018).

Occurrences of silver-bearing mineralization are quite common in the area of Sudetes Mountains in Poland (Lis and Sylwestrzak, 1986). The Ag-mineralization occurrences recorded in the literature are shown in Table 1. More Ag deposits and occurrences, as well as opportunities for comparison, can be observed within the Bohemian Massif in the Czech Republic. This area is famous for its numerous silver deposits mined in previous centuries, some of which are summarised in Table 2.

In the Boguszów baryte deposit only proustite has been noted without precise identification (Traube, 1888), as well as tetrahedrite with 3 wt.% Ag (Migaszewski, 1972). For many years silver ores were exploited in baryte veins in the Boguszów area. However, no quantitative results concerning the Ag-mineralization are available in the literature. This study describes the silver mineralization in the baryte veins and to provide precise chemical data on the silver minerals, especially for the TGM from the Boguszów baryte deposit.

LOCALITY AND GEOLOGICAL SETTING

The Boguszów baryte vein deposit (Segen Gottes Mine) is located on the south-west side of Chelmiec Hill (Fig. 1A), ~6 km to the west of Wałbrzych, close to the town of Boguszów Gorce. The baryte deposit is located in the Wałbrzych Depression, which is part of the fault-bounded, NW–SE trending Intra-Sudetic Depression, at the northern periphery of the Bohemian
Table 1

<table>
<thead>
<tr>
<th>Locality (type of mineralization)</th>
<th>Silver mineralization and Ag-enriched TGM</th>
<th>Generalized associated mineralization</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grudno</td>
<td>hydrothermal quartz-calcite-sulphide vein</td>
<td>freibergite [Ag₄(Cu₄Fe₆)Sb₂S₁₅], pyrargyrite [Ag₄Sb₂S₁₅]</td>
<td>quartz, calcite, arsenopyrite, pyrite, sphalerite, TGM, chalcopyrite, Cu, Pb, Sb minerals</td>
</tr>
<tr>
<td>Radzimowice</td>
<td>hydrothermal polymetallic veins</td>
<td>freibergite [Ag₄(Cu₄Fe₆)Sb₂S₁₅], acanthite [Ag₃S], gustavite [Ag₉PbSb₂S₁₉], treasurite [Ag₃Pb₂Sb₂S₁₅], hessite [Ag₃Te], electrum [Au₄Ag]</td>
<td>quartz, dolomite, calcite, siderite, ankerite, baryte, pyrite, arsenopyrite, chalcopyrite, galena, sphalerite, TGM, different sulphides and sulphasalts</td>
</tr>
<tr>
<td>Kletno</td>
<td>native silver, stromeyerite [AgCuS], miargyrite [AgSbS₂], argentite [Ag₃S], matildite [Ag₈Sb₈], naumannite [Ag₈Se₄], bohdanowiczite [Ag₈Se₄]</td>
<td>baryte, fluorite, calcite, uraninite, Fe oxides, Fe, Cu, Pb, Zn, Hg sulphides, bismuth sulphasalts</td>
<td>Banas and Mochnacka (2000)</td>
</tr>
<tr>
<td>Kowary</td>
<td>native silver [Ag], stromeyerite [AgCuS], proustite [Ag₄S₈], argentite [Ag₃S], pyrargyrite [Ag₄Sb₂S₁₅], matildite [Ag₈Sb₈]</td>
<td>calcite, dolomite, Fe oxides, uraninite, Fe, Cu, Pb, Zn, Bi sulphides and sulphasalts</td>
<td>Mochnacka and Banas (2000)</td>
</tr>
<tr>
<td>Rzędzyn</td>
<td>polymetallic mineralization in quartz veins and disseminated in schists and amphibolites</td>
<td>freibergite [Ag₄(Cu₄Fe₆)Sb₂S₁₅], Ag-rich tetrahedrite (up to 15.9 wt.% Ag)</td>
<td>pyrargyrite, cassiterite, pyrite, pyrhotite, chalcopyrite, cubanite, galena, sphalerite, bismuth sulphasalts and sulphoarcsulphides, TGM, Ag(Cu)²-PbBi(Sb) sulphasalts, Sn-bearing sulphasalts</td>
</tr>
<tr>
<td>Czarnów</td>
<td>polymetallic veins</td>
<td>argentite [Ag₃S], matildite [Ag₈Sb₈], treasurite [Ag₉Pb₂Sb₂S₁₉], hessite [Ag₃Te], Ag₂Bi sulphoarcsulphides</td>
<td>quartz, calcite, dolomite, arsenopyrite, chalcopyrite, pyrhotite, pyrite, galena, sphalerite, stibnite, cassiterite and other Cu-Bi sulphasalts and sulphasalts</td>
</tr>
<tr>
<td>Ciechanowice</td>
<td>polymetallic veins</td>
<td>acanthite [Ag₃S], Ag-amalgams, eugenite [Ag₁₋₂H₂O], native Ag, stromeyerite [AgCuS], argentite [Ag₃S], stephanite [Ag₈Sb₈], xanthoconite [Ag₈As₈], proustite [Ag₈As₈], polybasite [Cu₄Ag₄Cu₄Ag₄Sb₂S₃₁]</td>
<td>baryte, calcite, ankerite, löllingite, sallflonte, bornite, calchoit, TGM</td>
</tr>
<tr>
<td>Przecznica, Gierczyn</td>
<td>disseminated and vein-type cassiterite-polymetallic mineralization in chlorite-mica-quartz schists</td>
<td>pyrargyrite [Ag₈Sb₁₅]: Gierczyn and Przecznica, Ag-rich tetrahedrite (28–29 wt.% Ag): Przecznica</td>
<td>quartz, mica, chlorites, cassiterite, pyrhotite, sphalerite, chalcopyrite and different sulphides, arsenides and sulphasalts</td>
</tr>
<tr>
<td>Dzieńmorowice – Stary Julianów</td>
<td>hydrothermal polymetallic-baryte-quartz-calcite veins</td>
<td>freibergite [Ag₄(Cu₄Fe₆)Sb₂S₁₅], stephanite [Ag₈Sb₈]</td>
<td>baryte, quartz, calcite, galena, sphalerite, TGM, niccolite, smithite, cobaltite, pyrite, chalcopyrite, arsenopyrite, magnetite, uraninite</td>
</tr>
<tr>
<td>Zagórze Śląskie</td>
<td>hydrothermal polymetallic-baryte veins</td>
<td>argentopentlandite [Ag₄(Fe₆Ni₄)S₈]</td>
<td>baryte, chalcopyrite, galena, sphalerite, pyrhotite</td>
</tr>
<tr>
<td>Bystrzyca Górna</td>
<td>hydrothermal Ag-rich baryte-quartz veins</td>
<td>pyrargyrite [Ag₈Sb₁₅], stephanite [Ag₈Sb₈], miargyrite [Ag₈Sb₈], argentite [Ag₃S], dycrasite [Ag₈Sb₈], Ag-rich tetrahedrite, freibergite [Ag₄(Cu₄Fe₆)Sb₂S₁₅], zoubekite [Ag₈Pb₂Sb₂S₁₉], freiselbenite [Ag₈Pb₂Sb₂S₁₉], andorite VI [Ag₈Pb₂Sb₂S₁₉],</td>
<td>baryte, quartz, galena, sphalerite, greencock, chalcopyrite, TGM, bournonite, native antimony, Pb-Sb sulphasalts</td>
</tr>
<tr>
<td>Boguszów</td>
<td>hydrothermal Ag-rich baryte veins</td>
<td>Ag-enriched tetrahedrite-(Fe) and tetrahedrite-(Zn) (6.20 to 9.08 wt.% Ag), member of series &quot;freibergite-(Fe)&quot; and &quot;freibergite-(Zn)&quot;, pyrargyrite [Ag₈Sb₁₅], polybasite [Cu₄Ag₄Cu₄Ag₄Sb₂S₃₁]</td>
<td>baryte, quartz, carbonates, galena, sphalerite, TGM, chalcopyrite, pyrite, löllingite, gersdorffite, fluorite</td>
</tr>
</tbody>
</table>

Massif (Żelaźniewicz et al., 2011). The depression is filled with Carboniferous sediments: Calm facies (conglomerates and greywackes), Wabrycz and Biłaj Kamień units (coal-bearing lithostratigraphic units; Dziecić, 1971; Mastalerz, 1996; Kurowski, 1998). The sedimentary succession is divided by the Upper Carboniferous Chelmiec rhodacite lacyolith of Westphalian B/C transition age (310 ± 4 Ma) (Grocziński, 1965; Mastalerz and Mastalerz, 2000; Awdankiewicz and Kryza, 2010). The Boguszów baryte deposit is closely related to the NW-SE trending (strike-slip) fault-zone located in the NW part of the Chelmiec dome (Gruszczyk, 1952). Several baryte veins (Fig. 15) formed as a result of epithermal activity at a late stage of the subvolcanic activity and these veins cut the Chelmiec lacyolith and the surrounding sedimentary units (Gruszczyk et al., 1970).

In the Boguszów deposit, three main mineral assemblages related to baryte veins are observed: baryte-sulphides, baryte-fluorite and baryte-quartz (Gruszczyk, 1952). However, Paulo (1994) distinguished five ore mineralization stages there:

- quartz with Zn, Ag, Cu, Pb (minor As, Fe, Ni, Bi) sulphides;
- carbonates and hematite (Cu, Pb sulphides);
- baryte and fluorite (Pb, minor Cu and Zn sulphides);
- quartz, locally marcasite;
- fluorite leaching, oxidation, transparent baryte overgrowths.
Migaszewski (1972) studied and described different ore minerals from the hydrothermal veins (partly with baryte) and ore minerals located in the hydrothermally altered volcanic rocks: pyrite, sphalerite, tetrahedrite, chalcopyrite, galena, cobaltite and uraninite. Mining activity in the Boguszów area dates back to the 15th century, when silver-rich baryte-galena-tetrahedrite ores were exploited. Initially, the work was carried out by open pit methods. The first underground mine was opened in 1530 (Gruszczyk, 1952). Mining took place until 1755, when the lo-
Ore samples were collected in the old dumps close to Segen Gottes Mine in Boguszów. Samples were carefully checked macroscopically and >20 ore textures were chosen for microscopic study. Only samples containing silver mineralization were chosen for EPMA analysis. Silver minerals, main sulphides and sulpharsenides, were analysed using the JEOL Super Probe 8230 in the Laboratory of Critical Elements at the Faculty of Geology Geophysics and Environmental Protection, AGH-UST, Kraków Poland. The following operating conditions and standards were used: accelerating voltage 20 kV, beam current 20 nA (for sulphides and sulpharsenides) and beam current 10 nA (for Ag minerals), peak time 10–20 s, background time 10 s (5 s for Ag minerals) and a beam diameter 5 μm. The following wavelengths (to omit interference between the element spectral lines) were used: CdLα, ZnKα, CuKα, SkKα, SnLα, HgMα, FeKα, MnKα, AgLα, AsLα, SbLα, BiLα, TeLα, PbMα, SeLα, NiKα, CoKα (for sulphides and sulpharsenides); SkKα, CuKα, BiMα, AgLα, SbLα, SeLα, AsLα (for Ag minerals); BiMα, SbLα, ZnKα, CuKα, SkKα, HgMα, FeKα, AgLα, and AsLα for tetrahedrite. Natural mineral standards (FeS2, ZnS, PbS) and synthetic compounds (CdS, InAs, MnS, HgTe, PbTe, Sb2S3, Cu, Ag, Ni, Co, Se) were used for calibration. All interferences between the element spectral lines were calculated using autocorrections based on standards. The detection limits for analysed elements were as follows: for sulphides and sulpharsenides S – 0.01 wt.%, Zn – 0.03 wt.%, Fe – 0.03 wt.%, Cu – 0.02 wt.%, Ag – 0.02 wt.%, Cd – 0.02 wt.%, Hg – 0.02 wt.%, Co – 0.02 wt.%, for Ag minerals S – 0.02 wt.%, Sb – 0.09 wt.%, As – 0.12 wt.%, Cu – 0.05 wt.%, Ag – 0.35 wt.%, Bi – 0.06 wt.%, for tetrahedrite S – 0.02 wt.%, Sb – 0.07 wt.%, As – 0.01 wt.%, Cu – 0.04 wt.%, Ag – 0.02 wt.%, Zn – 0.04 wt.%, Fe – 0.03 wt.%, Hg – 0.06 wt.%, Bi – 0.05 wt.%

RESULTS

The main ore minerals in the samples studied are galena, sphalerite, tetrahedrite, pyrite and chalcopyrite (Fig. 2). Galena and sphalerite form small veinlets up to 1 cm in laminated baryte, as well as irregular aggregates up to several centimetres across in baryte breccia. Low-Ag tetrahedrite was also found as aggregates up to 1 cm in size disseminated in highly altered volcanic rocks or in baryte. Ag minerals and Ag-rich TGM mostly form inclusions or veinlets in galena up to a few hundreds of micrometres in size. Additionally, löllingite and gersdorffite occur as small, commonly zoned crystals in galena and tetrahedrite aggregates.

GALENA PbS

Galena is the main ore mineral of the baryte-sulphide ore. Galena forms aggregates up to several centimetres across, series of parallel veinlets in baryte veins, as well as breccia infillings cementing baryte and quartz fragments. Galena aggregates are intergrown with sphalerite, Ag-tetrahedrite and chalcopyrite (Fig. 2A, C, G). Some aggregates include abundant inclusions of silver-bearing mineral phases [members of the freibergite series: “freibergite-(Fe)” and “freibergite-(Zn)”, boronite, pyrrargyrite and polybasite; Fig. 2E]. Commonly, galena is replaced by various secondary minerals especially cerussite, less so covellite. Galena is chemically homogeneous and has a low content of trace elements.

Sphalerite crystals are irregularly distributed within baryte-quartz veins and are overgrown by galena and chalcopyrite (Fig. 3A). Sphalerite forms two generations where sphalerite II usually grows over primary massive aggregates of sphalerite I (Fig. 2G). The sphalerite has a generally low Fe content (up to 0.01 at% Fe) and is comparatively Cd-rich (up to 0.04 at% Cd) (Appendix 1). Intense brown internal reflections are observed, which are probably related to a lattice substitution of Cd for Zn. The highest Cd contents (0.03–0.04 at% Cd) are observed in the second generation of sphalerite. The Hg concentration in sphalerite reaches up to 0.01 at%, Cu reaches up to 0.01 at% Cd. The generalized empirical formula is: Zn0.95-0.99Cd0.00-0.04Fe0.00-0.01Hg0.00-0.01Sb0.00-0.01.

TETRAHEDRITE GROUP MINERALS

At Boguszów, there are four generations of TGM defined according to textural characteristics and silver content (Fig. 3A). The nomenclature follows the new classification of TGM (Biagioni et al., 2020a):
1. low-Ag tetrahedrite-(Zn) (Ag: 0.22–0.6 at% Ag)
2. Ag-enriched tetrahedrite-(Zn) and Ag-enriched tetrahedrite-(Fe) (Ag: 0.71–1.45 at% Ag)
3. members of the freibergite series: “freibergite-(Fe)” and “freibergite-(Zn)” (Ag: 3.21–3.48 at% Ag)
4. member of the freibergite series: “freibergite-(Fe)” (Ag: 5.32–5.78 at% Ag).

Low-Ag tetrahedrite-(Zn) is observed as idiomorphic crystals up to 5 mm in size without any inclusions and without other sulphides association (Fig. 2B). Representative analyses of the tetrahedrite-(Zn) are shown in Appendix 2. The low-Ag tetrahedrite-(Zn) is characterized by small variation in Cu and Ag concentrations. Individual results mostly vary in As content (from 0.57 to 1.74 at% As). This generation of TGM is the zinc member of the tetrahedrite series (Fig. 4B). A generalized formula for low-Ag tetrahedrite-(Zn) based on 16 cations is:
(Cu0.37-0.80Ag0.22-0.60Zn1.16-1.72Fe0.20-0.72Hg0.02-0.05)2+11.95-12.01(Sb2.24-3.47As0.07-1.72Bi0.01-0.03)3+3.99-4.05O0.98-1.03S0.10-0.13. Similar low-Ag tetrahedrite with 3 wt.% of Ag was reported by Migaszewski (1972) from veinlets criss-crossing altered volcanic rock.

AG-ENRICHED TETRAHEDRITE-(Zn) • AG-ENRICHED TETRAHEDRITE-(Fe)

Ag-enriched tetrahedrite-(Zn) and Ag-enriched tetrahedrite-(Fe) are intergrown with galena and chalcopyrite, as well as
Fig. 2. Optical (reflected light, 1P) (A–E) and BSE images (F–H) illustrating the main features of mineral assemblages

A – galena – Ag-enriched tetrahedrite – sphalerite aggregate with chalcopyrite; B – single idiomorphic low-Ag tetrahedrite-(Zn) crystal in baryte; C – galena – Ag-enriched tetrahedrite aggregate with pyrargyrite and löllingite-gersdorffite inclusions; D – pyrargyrite – chalcopyrite aggregate at the edge of galena; E – linear inclusions of pyrargyrite and members of the freibergite series in galena; F – zonation in Ag-enriched tetrahedrite crystal reflecting iron and zinc abundances; G – galena-sphalerite aggregate with some secondary Cd-enriched zones in sphalerite; H – löllingite-gersdorffite inclusions in galena; Ag-Ttr – Ag-enriched tetrahedrite; Brt – baryte; Ccp – chalcopyrite; Frb – members of the freibergite series; Gn – galena; Grd – gersdorffite; Lo – löllingite; Low-Ag Ttr – low-Ag tetrahedrite-(Zn); Prg – pyrargyrite; Sph – sphalerite
occuring as irregular aggregates up to 0.5 mm across (Fig. 2A, C, H). Some aggregates are enriched in tellurite and tellurite inclusions up to 20 μm in size (Fig. 2C). Results of chemical analysis of this generation of TGM are shown in Appendix 2. As in the previous generation, a similar trend of the As-Sb substitution is observed (Fig. 3B). Microprobe analyses indicate a wide range of Zn-Fe substitution and a dominance of the zinc member of the tetrahedrite generation (Fig. 4B). Element ranges in the D position in the TGM are Fe – 0.26–1.15 apfu, and Zn – 0.8–1.79 apfu respectively. A generalized formula can be expressed as: (Cu₉.₆₅₋₉.₃₃)₆₋₇₁₋₇₉(Zn₀.₈₀–1.₇₉)₆₋₇₁₋₇₉Fe₁₋₂₆₋₁₇₉Hg₀.₀₀–₀.₀₅Zn₂₋₇ₒ₋₇₉(Sb₂₋₇₅₋₇₉As₁₋₇ₒ₋₇₉)₀.₀₁₋₀.₀₉₋₇₉S₁₋₃₋₆₋₁₆₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃. The results are shown in Appendix 2. A generalized formula based on 16 cations can be expressed as: (Ag₂₋₇₉Cu₁₋₄₆₋₇₃Fe₁₋₆₆₋₁₇₉Hg₁₋₅ₐ₋₁₄₋₅ₐZn₀.₀₀–₀.₀₅)₂₋₇₉(Sb₂₋₇₅₋₇₉As₂₋₇ₙ₋₇₉)₀.₀₁₋₀.₀₉₋₇₉S₁₋₃₋₆₋₁₆₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃. The pyrargyrite investigated mostly occurs as inclusions up to 50 μm across in galena (Fig. 2E). Pyrargyrite intergrowths with chalcopyrite (up to 100 μm across) are also present (Fig. 2D). They are characterized by uniform chemical composition (Appendix 1). Generally, pyrargyrite is practically arsenic-free. Only isolated pyrargyrite grains are characterized by notably higher As concentrations (~2 wt.%). A generalized pyrargyrite formula based on 4 cations is: (Ag₂₋₇₉Cu₁₋₄₆₋₇₃Fe₁₋₆₆₋₁₇₉Hg₁₋₅ₐ₋₁₄₋₅ₐZn₀.₀₀–₀.₀₅)₂₋₇₉(Sb₂₋₇₅₋₇₉As₂₋₇ₙ₋₇₉)₀.₀₁₋₀.₀₉₋₇₉S₁₋₃₋₆₋₁₆₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃.

MEMBERS OF THE FREIBERGITE SERIES:
"FREIBERGITE-(Fe)" AND "FREIBERGITE-(Zn)"

Members of the freibergite series, “freibergite-(Fe)” and “freibergite-(Zn)”, occur as elongated inclusions up to 100 μm long along galena cleavage planes, as well as tiny irregular inclusions (Fig. 2E). The compositional variation of this tetrahedrite generation is shown in Appendix 2. This generation tends to be As-poor, As – up to 0.002 apfu. Consequently, Sb content is relatively uniform and ranges between 3.98–4.12 apfu. Most of the freibergites are “freibergite-(Zn)”, which is currently not a defined member of the freibergite series (Biagioni et al., 2020a). Zinc concentration ranges from 0.11 to 1.17 apfu, Fe content is generally lower and reaches up to 0.98 apfu (Fig. 4B–D). Moreover, some of the EPMA analyses show relatively high mercury contents of up to 0.75 apfu. The highest Hg content was measured in freibergite-(Fe), where Fe contents exceed Zn. Hg decreases with increasing Zn content. Additionally, Hg-enriched freibergite has the lowest silver content in this generation of freibergites (3.26–3.32 apfu). Comparative readings of Zn versus Fe+Hg (Fig. 4B) and Zn versus Fe+Hg+(Cu+Ag) cross-plots (Fig. 4C) show that copper in position C is common in this TGM generation. The generalized formula for “freibergite-(Fe)" and “freibergite-(Zn)" is: (Cu₉.₅₆₋₇₉Ag₂₋₄₆₋₇₃Zn₀.₁₁–₁.₁₇₋₇₉Fe₆₋₇₉₋₇₉Hg₀.₀₁₋₀.₇₅₋₇₉Sb₂₋₇₅₋₇₉B₁₋₂₋₁₆₋₁₄₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃₋₁₂₋₁₃. This mineral is a minor phase and occurs as inclusions related to the cleavage planes in galena crystals. Most of the bournongite inclusions in samples from Boguszów are too small.
to be quantitatively analysed by EPMA due to their fine grain size (up to 1–3 μm). It was possible to measure only some inclusions, the chemical composition is close to the ideal formula without any significant substitutions.

**LÖLLINGITE FeAs**

Löllingite occurs as idiomorphic crystals up to 10 μm in size within galena and Ag-enriched tetrahedrite aggregates (Fig. 2C, H). A summary of the analytical results available for löllingite are shown in Appendix 1. In comparison with stoichiometric löllingite, the löllingite from Boguszów is Fe-depleted (0.67–0.91 apfu), besides Co (0.03–0.24 apfu) and Ni (up to 0.16 apfu) enrichment.

**GERSDORFFITE NiAsS**

Gersdorffite appears as thin rims (up to several μm thick) around löllingite crystals (Fig. 2C, H). The compositional variation of gersdorffite is shown in Appendix 1. Gersdorffite is
generally enriched in Co (0.11–0.37 apfu), less in Fe (0.07–0.22 apfu). Common substitutions between cobalt, nickel, and iron are observed in the gersdorffite from the Boguszów. The generalized empirical gersdorffite formula is: 

\[(Ni_{0.53-0.81}Co_{0.11-0.27}Fe_{0.07-0.22})_2\delta^{-1}As_{0.03-1.14}Sb_{0.09-0.98}\] 

Transition zones between löllingite crystals and gersdorffite rims are observed, but are too small to be measured by EPMA.

**DISCUSSION**

**SILVER MINERALIZATION IN SUDETES AND BOHEMIAN MASSIF**

The Sudetes in Poland include ~30 recorded baryte veins (Paulo, 1994), the highest rate of occurrence being observed in the Sowie Mountains and the Intra-Sudetic Depression. Polymetallic Pb-Zn-Ag mineralization is associated with a large part of these veins. Mining, which goes back to medieval times, was focused towards the silver-rich ores. However, previous reports of silver minerals and Ag-rich TGM in the old literature do not contain reliable chemical data, including from Boguszów (Traube, 1888; Migaszewski, 1972) and Dziecimorowice (Petrascheck, 1933). Direct comparison is possible only with hydrothermal mineralization from Zagórze Śląskie (Piestrzyński and Kowalik, 2015) and Bystrzycia Góra (BG) (Pršek et al., 2019), which are located within the Sowie Mountains. For example, polymetallic mineralization in the baryte veins from Zagórze Śląskie is characterized by a higher abundance of Cu minerals. More mineralogical similarities with the mineralization studied can be found in polymetallic Ag-Sb-Pb-(Cd) mineralization related to baryte veins at BG. Pršek et al. (2019) reported the presence of e.g. silver-enriched TGM, Ag-Sb-S, Ag-Pb-S and Pb-Sb sulphosalts (Table 1). In contrast to textures of Ag mineralization from Boguszów (elongated inclusions in galena), at BG silver mineralization forms veinlets and disseminations in a fine-grained dark baryte-quartz matrix. In contrast to the Boguszów hydrothermal system, in BG arsenic is absent from the entire paragenetic sequence, the mineralization being extremely Sb-rich. According to Pršek et al. (2019) a smoother transition of Cu-“Ag” substitution in TGM was recognized at BG. Chemical zonation regarding the distribution of Ag abundances is observed, freibergite-(Fe) rims around lower-Ag TGM being common at this locality. At Boguszów four particular TGM generations have been distinguished (Fig. 3A). As Pršek et al. (2019) state about BG, the former tetrahedrite (related to the early stage – base metal mineralization) was dissolved by younger Ag-rich fluids, which are responsible for unusual Ag-Sb-Pb-(Cd) mineralization. In comparison to the mineralization from BG, textural features in ores from Boguszów indicate an increase in Ag-rich phases [freibergite-(Fe), pyrrhotite and polybasite] during the younger epithermal stages. As previously mentioned, in the past, more silver mines were active within the Bohemian Massif (Table 2). Silver was recovered mainly from Ag-rich TGM and Ag-Sb sulphosalts, which occur in baryte – quartz ± carbonate veins. In general, Ag-bearing tetrahedrite or freibergite is one of the most important sources of silver in these silver-bearing mining districts in the Czech Republic and Poland. The accompanying silver minerals are variable and the presence of individual minerals depends on various ore-forming conditions as well as the local geochemical source of mineralization.

**MERCURY IN TETRAHEDRITE GROUP MINERALS**

The presence of mercury in the TGM from Boguszów is restricted to few samples. The highest enrichment is observed in member of the “freibergite-(Fe)” series, which is Sb-rich and Zn-depleted – similarly to the hybrid massive sulphide-epithermal Eskay Creek deposit in Canada (Grammatikopoulos et al., 2005). Hg-Ag tetrahedrite from Eskay Creek (Hg: 0.12–1.54 apfu; Ag: 1.11–3.66 apfu – based on 16 cations) is associated with sphalerite-tetrahedrite, cinnabar, galena, stibnite and Pb-Sb sulphosalts. Another occurrence of Hg-Ag tetrahedrite from Chirovovtsi Ag-Pb (Bulgaria) was reported by Atanasov (1975). Ag-Hg rich tetrahedrite (Hg: 1.82–1.86 apfu; Ag: 2.88–3.13 apfu – based on 16 cations) is associated with the pyrite-cinnabar stage and forms rims around cinnabar agglomerates. Mercury-dominant tetrahedrite group minerals (Biagioni et al., 2020a) are common in the mineralization rich in mercury and have been reported from many localities (e.g., Mozgov et al., 1979; Arti and Diamond, 1998; Foit and Ulbricht, 2001; Karanović et al., 2003; Krsimer et al., 2011; Velebil, 2014; Števko et al., 2015; Biagioni et al., 2020b). Tetrahedrite enriched in Hg is generally Ag-free or Ag-low and it is associated with Cu, Hg, As, Sb, Bi minerals in quartz or quartz-carbonate-baryte veins as reported worldwide. Examples of the chemical composition of Ag- and Hg-rich TGM are shown in the ternary Ag versus Zn and Zn versus Fe versus Hg diagrams (Fig. 5). The most Ag-enriched Hg-rich TGM tend to be Zn-poor.

**Ni-Co ASSOCIATION**

Nickel and cobalt minerals are present in various hydrothermal occurrences and deposits. Especially characteristic is the “five-element vein type” mineralization (“Ag-Co-Ni-As-Bi type”) (Kissin, 1992; Marki et al., 2016; Scharrer et al., 2019). Ni-Co enrichment in hydrothermal mineralization may also be related to leaching of these elements by hydrothermal fluids from the surrounding ultramafic rocks (Doliček et al., 2019a). In the Boguszów baryte deposit the Ni-Co assemblage is represented by tiny aggregates of Co-enriched löllingite and gersdorffite. Additionally, small isometric inclusions of cobaltite in tetrahedrite up to 15 μm in size were reported by Migaszewski (1972). Metals in this assemblage were probably sourced from the ultramafic basement of the Intra-Sudetic Ophiolite, as was proposed for hydrothermal veins in the Moravo-Silesian Culm from the Řepová – ultramafic Zábřeh Crystalline Complex, where a Ni-Co assemblage is associated with base metal +Ag-Hg-Au mineralization (Doliček et al., 2019a).

**CONCLUSIONS**

1. Silver in the Boguszów baryte deposit occurs in the form of its minerals: Ag-Sb sulphosalts (pyrrhotite, polybasite) and tetrahedrite group minerals (TGM). The composition of these minerals, which form elongated inclusions in galena aggregates, was determined using an electron microprobe.
2. Other ore minerals found are galena, sphalerite, pyrite, chalcopyrite, boumouite, löllingite and gersdorffite.
3. Four generations of the TGM were distinguished according to textural characteristics and Ag concentrations:

- 1 – low-Ag tetrahedrite-(Zn) (Ag: 0.22–0.6 apfu),
2 – Ag-enriched tetrahedrite-(Zn) and Ag-enriched tetrahedrite-(Fe) (Ag: 0.71–1.45 apfu),
3 – members of the freibergite series: “freibergite-(Fe)” and “freibergite-(Zn)” (Ag: 3.21–3.48 apfu),
4 – member of the “freibergite-(Fe)” series (Ag: 5.32–5.78 apfu).
4. Similar Ag mineralization occurrences related to Ag-Pb-Sb minerals are known from several localities in the Sudetes and the Bohemian Massif.
5. The Boguszów baryte deposit is one of the few localities known in the world with Hg-rich members of freibergite series.
6. The presence of cobalt-enriched löllingite and gersdorffite may indicate leaching of Ni and Co by hydrothermal fluids from the ultramafic basement.

Acknowledgements. We are grateful to G. Kozub-Budzyń from the Laboratory of Critical Elements at AGH-UST for help during EPMA data collection. We are also grateful to the reviewers, J. Sejkora and S. Mikulski, whose comments helped us to improve the manuscript. This work is part of the research program financed by the AGH University of Science and Technology statutory grant No. 11.11.140.320.

REFERENCES

Foit Jr, F.F., Ulbricht, M.E., 2001. Compositional variation in mercurian tetrahedrite–tennantite from the epithermal deposits...


Scharrer, M., Kreissl, S., Markl, V., 2005. The mineralogical variability of hydrothermal native element-arsenic (five-element)


Geochemistry and geochronology of the Jawornik granitoids, Orlica-Śnieżnik Dome, Sudetes, Poland

Dawid BIAŁEK1, *

1 University of Wrocław, Institute of Geological Sciences, pl. M. Borna 9, 50-204 Wrocław, Poland


Associate Editor: Leszek Krzemiński

The Jawornik granitoids intrude, in vein-like form, a sequence of a polymetamorphic metavolcanic and metapelite rocks of the Orlica-Śnieżnik Dome, Sudetes, Poland. This paper provides whole-rock geochemical data, sensitive high-resolution ion microprobe (SHRIMP) U-Pb zircon geochronological data as well as 40Ar-39Ar age determinations to constrain the genetic and temporal relationships of the different rock types forming these veins. Based on macroscopically visible features of the granitoids and their relationship with tectonic structures visible in the country rocks, four varieties of the Jawornik granitoids have been distinguished: amphibole- and biotite-bearing granites (HBG), biotite-bearing granites (BG), biotite- and muscovite-bearing granites (BMG) and muscovite-bearing granites (MG). The Jawornik granitoids as a whole show a limited but significant variation in major element chemical composition, with SiO₂ ranging from 65 to 76 wt.% (average 69.16 wt.%, n = 24). They are subalkalic, peraluminous and calc-alkaline [average A/CNK = 1.07, average (Na₂O + K₂O) = 7.75, average (Fe₂O₃)/(Fe₂O₃ + MgO) = 0.59]. Close inspection of their geochemical parameters showed that the samples investigated can be subdivided into two groups. The first group, the HBG, BG, and BMG varieties, comprising most of the granitoids in the Złoty Stok-Skrzynka Tectonic Zone, were formed by melting of greywackes or/and amphibolites. The MG, belonging to the second group, were formed by partial melting of a more felsic source. The HBG yielded a zircon U-Pb age of 351 ±1.3 Ma and well-defined 40Ar-39Ar plateau ages for hornblende (351.1 ±3.9 Ma) and coexisting biotite (349.6 ±3.8 Ma), indicating probably the oldest magmatic event in this region. Zircons from the MG, the youngest rock variety on the basis of their relationship with the tectonic structures in the host rocks, yielded a U-Pb age of 336.3 ±2.4 Ma, though based on three points only. The biotites and muscovites from the BMG have 40Ar-39Ar plateau ages of 344.1 ±4.7 Ma and 344.6 ±3.8 Ma, respectively. These data, in combination with already published isotopic ages, suggest that the Jawornik granitoids intruded host rocks of the Orlica-Śnieżnik Dome in three stages, at ~350, ~344 and ~335 Ma.

Key words: Jawornik granitoids, geochemistry, geochronology, Sudetes, Variscan granitoids.

INTRODUCTION

The Sudetes, located in southwestern Poland, northeastern Bohemia and northern Moravia, represent a small portion of the Variscan Orogenic Belt in Europe and form the NE part of the Bohemian Massif (Fig. 1). Geological units, belonging to all four major lithotectonic domains of the Bohemian Massif (i.e. Saxothuringian, Teplá-Barrandian, Moldanubian and Brunnovistulian domains), make up the complex structural mosaic of the Sudetes (Matte et al., 1990; Cymerman et al., 1997; Franke, 2000; Franke and Zelaźniewicz, 2002; Mazur et al., 2006, 2015; Schulmann et al., 2014). The assembly of these units occurred during Late Devonian to Early Carboniferous terrane collisions (e.g., Matte et al., 1990; Cymerman et al., 1997; Aleksandrowski and Mazur, 2002). The Variscan granitoids form a portion of the rock inventory in all of them. They differ in age, composition and their tectonic context. The Bohemian Massif is an example of a hot orogen with numerous compositionally diversified granitoid plutons. The plutonism was active for nearly 80 My, and on the basis of their tectonic settings, age and petrogenesis, four groups of plutons have been distinguished (Zak et al., 2014). The oldest (~375 Ma), volumetrically small, granitoid bodies, are subduction-related, connected with early stages of plate collision. Plutons belonging to the next two groups (354–346 Ma and 340–335 Ma) were emplaced during consecutive phases of orogenic deformation. In the fourth group there are plutons emplaced during final stages of the Variscan orogeny (330–320 Ma) and post-orogenically (~300 Ma). The largest Sudetic plutons – the Karkonosze Pluton, Strzegom-Sobótka Massif, Żulowá Pluton, and small intrusions that crop out in the Strzelin Massif, emplaced on the periphery of the Variscan orogen, can be classified as late- to post-tectonic (Oberc-Dziedzic and Kryza, 2012; Kryza et al., 2014; Laurent et al., 2014; Tumiak et al., 2014). Older and smaller granitoids of the central Sudetes are spatially

* E-mail: dawid.bialek@uwr.edu.pl
Received: March 6, 2020; accepted: July 30, 2020; first published online: October 30, 2020