Ag-Pb-Sb Sulfosalts and Se-rich Mineralization of Anthony of Padua Mine near Poličany—Model Example of the Mineralization of Silver Lodes in the Historic Kutná Hora Ag-Pb Ore District, Czech Republic

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Abstract: Significant selenium enrichment associated with selenides and previously unknown Ag-Pb-Sb, Ag-Sb and Pb-Sb sulfosalts has been discovered in hydrothermal ore veins in the Anthony of Padua mine near Poličany, Kutná Hora ore district, central Bohemia, Czech Republic. The ore mineralogy and crystal chemistry of more than twenty silver minerals are studied here. Selenium mineralization is evidenced by a) the occurrence of selenium minerals, and b) significantly increased selenium contents in sulfosalts. Identified selenium minerals include aguilarite and selenides naumannite and clausthalite. The previously unknown sulfosalts from Kutná Hora are identified: Ag-excess fizelyite, fizelyite, andorite IV, andorite VI, unnamed Ag-poor Ag-Pb-Sb sulfosalts, semseyite, stephanite, polybasite, unnamed Ag-Cu-S mineral phases and uytenbogaardtite. Among the newly identified sulfides is argyrodite; germanium is a new chemical element in geochemistry of Kutná Hora. Three types of ore were recognized in the vein assemblage: the Pb-rich black ore (i) in quartz; the Ag-rich red ore (ii) in kutnohorite-quartz gangue; and the Ag-rich ore (iii) in milky quartz without sulfides. The general succession scheme runs for the Pb-rich black ore (i) as follows: galena – boulangerite (– jamesonite) – owyheeite – fizelyite – Ag-exces fizelyite – andorite IV – andorite VI – freieslebenite – diaphorite – miargyrite – freibergite. For the Ag-rich red ore (ii) and ore (iii) the most prominent pattern is: galena – diaphorite – freibergite – miargyrite – pyragyrite – stephanite – polybasite – acanthite. The parallel succession scheme progresses from Se-poor to Se-rich phases, i.e., galena – members of galena – clausthalite solid solution – clausthalite; miargyrite – Se-rich miargyrite; acanthite – aguilarite – naumannite. A likely source of selenium is in the serpentinized ultrabasic bodies, known in the area of “silver” lodes in the South of the ore district, which may enable to pre-concentrate selenium, released into hydrothermal fluids during tectonic events. The origin of the studied ore mineralization is primarily bound to the youngest stage of mineralization of the whole ore district, corresponding to the Ag-Sb sequence of the ‘eb’ ore type of the Freiberg ore district in Saxony (Germany) and shows mineralogical and geochemical similarities to low-sulfidation epithermal-style Ag-Au mineralization.

Keywords: Ag-Pb-Sb sulfosalts; selenium-rich mineralization; Kutná Hora; clausthalite; naumannite; andorite group; argyrodite; Ag-Sb(-Au) alloys; acanthite – aguilarite; succession
1. Introduction

Kutná Hora was one of the best-known mining centres in Europe in the Middle Ages. In the first stage of mining (in the 13th and 14th century), the ores of silver-rich lodes in the southern part of the Kutná Hora ore district (Figure 1a) were mined extensively. By means of the so-called fire-setting mining technique 500 m depth below the surface was reached as early as before the end of 14th century [1,2]. Before the end of the 15th century, mining activity moved from the silver-rich southern part of the Kutná Hora ore district (especially Oselské pásma Lode) to the northern part of this district, which had silver-bearing sulfide “pyrite-rich” ores (especially Staroˇ ceské terrywallaceite, vikingite, treasurite, eskimoite, erzwiesite, izoklakeite, aramayoite [22,23] and new minerals from northern lodes include canfieldite [18], gustavite [19,20] and matildite [21]. The pyrite-rich assemblage has recently yielded silver [9],Au-rich silver and Au-bearing dyscrasite [11]. No selenium minerals have been known, no selenium contents above detection limit determined.

The knowledge of mineralogy of ore veins in the southern silver-rich part of the Kutná Hora ore district has so far been incomplete. Mining in this historically important part of the ore district ended in the 16th century and later explorations were carried out only on a very limited scale [3–8]. Therefore, mineralogical research of this part of the ore district had to rely only on occasional finds of primary mineralization on medieval mine dumps, mostly localized in areas built up by medieval town [8], but still partly preserved south of the historic centre of the town. Known silver minerals from southern lodes of the ore district include acanthite [9,10], allargentum [9,11], diaphorite [12,13], freibergite [13], freieslebenite [14], miargyrite [13,15], owyheeite [16], proustite [13], pyragyrite [13], pyrostilpnite [17], stephanite [11], silver [9],Au-rich silver and Au-bearing dyscrasite [11]. No selenium minerals have been known, no selenium contents above detection limit determined.

In northern lodes, the following silver minerals not occurring in southern lodes were described: canfieldite [18], gustavite [19,20] and matildite [21]. The pyrite-rich assemblage has recently yielded a rich suite of Ag-Pb-Bi-Sb sulfosalts. Recently identified minerals from northern lodes include terrywallaceite, vikingite, treasurite, eskimoite, erzwiesite, izoklakeite, aramayoite [22,23] and new mineral staroˇ ceské tite [24].

Figure 1. (a) Map of the Kutná Hora ore district with major ore lodes, adapted from Malec and Pauliš [25]. Each lode (“pásma” in Czech, “Zug” in German) consists of several veins. (b) map of Anthony of Padua mine, Kutná Hora, adapted from Koutek and Kutina [26]. The blue-marked sections are ore-mineralized.
The small Anthony of Padua Mine, located near the village of Poličany in the southern part of the Kutná Hora ore district, has been preserved to this day owing to the renewed exploration mining during the World War II. Thus, the mine represents a unique opportunity to study in detail the mineralogy of Ag-rich ores both in dump material and also in situ, sampled in the ore veins uncovered inside the mine. Therefore, it is a very appropriate model example, providing a large abundance and variety of new information on the mineralogy of the southern part of the Kutná Hora ore district, including the newly discovered, previously unknown selenium mineralizations from Kutná Hora.

2. Geological Setting

2.1. Kutná Hora Ore District

The Kutná Hora Ag-Pb-Zn ore district (60 km east of Prague, Central Bohemia, Czech Republic) represents a hydrothermal vein type mineralization of Variscan age [26]. The ore district covers the area of 10 × 5 km in N-S direction. Ore veins are clustered in so-called ore zones or lodes (“pásma” in Czech), each 1 to 3 km in length and 100–500 m in width (Figure 1a). A detailed description of the geological and mineralogical situation of the Kutná Hora ore district is given in [25–27]. The genetical, geological, mineralogical and chemical similarities of the ore districts of Kutná Hora and Freiberg (Germany) have been studied and pointed out by several authors, e.g. [28,29].

In general, two mineral assemblages are present in the ore district: one “silver-rich”, developed in gneisses of the Varied unit of the Kutná Hora Crystalline Complex in the south, and the other “pyrite-rich” in gneisses and migmatites of the Malšín unit in the north [25,26]. The silver-rich assemblage consists mainly of miargyrite, pyrargyrite, freibergite, freieslebenite, diaphorite, allargentum, native silver, galena, pyrite, sphalerite, berthierite and Pb-Sb(-Ag) sulfosalts (boulangerite, jamesonite, owyheeite) in quartz–kutnohorite gangue [25,27].

The pyrite-rich assemblage comprises pyrite, arsenopyrite, sphalerite, Ag-bearing galena, pyrrhotite, marcasite, chalcopyrite, stannite, freibergite and Pb-Sb-Bi-Ag) sulfosalts in quartz gangue without kutnohorite. The presence of Bi and Sn (each from a different mineralization sequence) is typical, while it is completely absent in the former, silver-rich assemblage. The pyrite-rich assemblage yields a rich suite of Ag-Pb-Bi-Sb sulfosalts, recently studied by Pažout [22,23].

2.2. Anthony of Padua Mine Near Poličany

Anthony of Padua mine is situated south of Kutná Hora near the village of Poličany in the valley of the Vrchlice stream, about 200 m SSW of Kruchta Mine, which is the southernmost historically documented mine of the Oselské pásma Lode, the largest “silver lode” of the medieval Kutná Hora ore district. Geologically and mineralogically, the mine belongs to the Oselské pásma Lode. The adit of the Anthony of Padua mine (situated at GPS: 49°55.77858’ N, 15°15.29307’ E) accesses ore veins that belong to the southern “silver-rich” Oselské pásma Lode (Figure 1a).

The first mine workings in this area began probably already around 1300; written references about mining activity come from 1752–1755 [7,30,31] and 1769–1770 [32]. The last exploration works in the adit were undertaken in 1943–1945 [32]; at present, this abandoned mine is still partially accessible.

Ore veins of the Anthony of Padua Mine are developed in gneisses of the Varied unit of the Kutná Hora Crystalline Complex, namely in protoreozoic medium to strongly migmatized double-mica paragneisses with transition to migmatites with interbeds of muscovite-biotite othogneisses; the composition of wall rock has no or little influence on hydrothermal mineralization [32]. These rocks are classed as belonging to the Šternberk-Čáslav Group established by [26] and [33]. In the central part of the Kutná Hora ore district, the rocks of the Crystalline unit are covered by Cretaceous and later Quaternary sediments, while in the valley of the stream of Vrchlice near Poličany Cretaceous sediments are missing and Quaternary sediments are denudated.

Anthony of Padua mine accesses five ore veins with strings in a zone or area 30–40 m wide (Figure 1b), with a typical thickness of 20 to 50 cm (occasionally bulging to 1 m) and N–S to NNE–SSW
direction. Therefore, some veins intersect, or are considered to be strings. Some dip 60 to 85° to the E, other to the W [32]. Vein gangue consists of quartz and kutnohorite with disseminated or massive sulfides. The mineralogy of ores found in Anthony of Padua mine was systematically studied for the first time by Koutek and Kutina [32], which was followed by another paper by Kutina [34], presenting the results of semi-quantitative chemical analyses. The results of shorter papers are summarized in [35] and newly in concise articles of [25,27,36]. Known silver minerals from the Anthony of Padua mine include: miargyrite, pyrargyrite, freibergite, diaphorite, freieslebenite and silver. Until now, only contents of Se up to 0.14 wt.% were found [35] in galena from Anthony of Padua mine.

3. Sampling and Analytical Methods

The studied ore samples were collected in situ the adit of Anthony of Padua mine (Figure 1b), from spots described in Section 4.1. Samples for microscopy and following laboratory study were prepared as polished sections 2.54 cm in diameter, mounted in resin and polished with diamond suspensions. The ore minerals and textures were studied in reflected light using a Nikon Eclipse ME600 polarizing microscope in the National Museum, Prague.

Seventy polished sections, prepared from a representative number of ore specimens collected during field work in 1999–2015, were investigated microscopically and subsequently analysed on two different electron microprobes (3000 point analyses altogether). Quantitative chemical analysis was performed with Cameca SX electron microprobe (EPMA, National Museum, Prague), WDS analysis, operated at 25 kV, 20 nA, and a beam diameter of 2 µm. The following standards and X-ray lines were used: Ag (AgLα), CdTe (CdLα), CuFeS2 (CuKα), FeS2 (FeKα, SKα), NiAs (AsLβ), PbCl2 (ClKα), Pb3 (PbMα), PbSe (SeLβ), Sb2S3 (SbLα) a ZnS (ZnKα). Raw intensities were converted to the concentrations of elements using automatic “PAP” matrix-correction software. The second portion of polished sections (incl. Au-rich silver) was analysed with the electron probe microanalyser JEOL JXA-8530F at Institute of Petrology and Structural Geology, Faculty of Natural Sciences, Charles University, Prague. Accelerating voltage was 20 kV, beam current 20 nA and electron-beam diameter 1 µm. The following standards and X-ray lines were used: Au (AuLα), Ge (GeLα), cuprite (CuKα), cinnabar (HgLα), Bi2Se3 (SeLα), Ag (AgLα), Sb2Te3 (TeLα), stibnite (SbLα) and marcasite (SKα). Measured data were corrected using ZAF method.

Peak-counting times were 20–30 s and one-half of the peak time was used for each background. The contents of the above-listed elements, which are not included in the tables, were analysed quantitatively, but their contents were below the detection limit (ca. 0.01–0.04 wt.% for individual elements).

4. Mineralogy and Mineral Chemistry—Results

4.1. Characterization of Ore Mineralization of Anthony of Padua Mine

The majority of the studied material comes from Vein B (Figure 1b), with a thickness of 20–60 cm, NNE–SSW direction and dipping 65° to the East. Two basic kinds of ore mineralization were found in this vein: (i) Pb-rich (so called “black ore”) and (ii) silver-rich (so called “red ore”), differing in associated minerals, prevailing and present elements and gangue minerals. Black ore (i) is formed by massive or disseminated grain aggregates (up to the size of 15 cm) consisting of galena, miargyrite, massive Pb-Sb sulfosalts (boulangerite, jamesonite) and pyrite in quartz gangue and fewer carbonates (kutnohorite). Accessory minerals include freibergite, sphalerite, Ag-Pb-Sb sulfosalts (diaphorite, freieslebenite, minerals of the andorite series, owyheeite). Selenium is present in members of galena–clausthalite solid solution.
On the other hand, the Ag-rich red ore (named after its marked colour)—ore (ii)—consists of grains of miargyrite up to 5 centimetres across, associated with pyrargyrite, freibergite, with crystals up to 5 mm in occasional cavities, small metallic outgrowths of native silver up to 3 mm, coarse-grained sphalerite and massive pyrite in kutnohorite and quartz. Ag-Pb-Sb sulfosalts are rare or non-present (no andorite group minerals). Accessory minerals include aguilarite, selenides naumannite and clausthalite, high-grade silver minerals (stephanite, acanthite), germanium is present in argyrodite and Au occurs as Au-rich silver (electrum) and Au-rich dyscrasite.

Another portion of the studied material, representing ore (iii), comes from the intersection of the vein I and the vein A (Figure 1b); the main vein I, with a thickness of 20–80 cm, N–S direction and dipping 65–80° to the E, cuts and shifts by several decimetres a diagonal vein A with the thickness of 20–40 cm, NE–SW direction and with dips of 35–65° to the SE. The prevailing mineral is miargyrite in milky white quartz, the sparse associated base sulfide (if it occurs) is pyrite. Miargyrite forms massive grains, bands and veinlets up to several cm in size and well-developed crystals in quartz cavities, usually several mm in size. The maximum size of individual crystal exceeds 1 cm. Often, thin red fillings of miargyrite in fractures and fissures in quartz occur. Miargyrite is accompanied by less frequent pyrargyrite, freibergite, pyrostilpnite, diaforite and freieslebenite.

4.2. Pb-Sb-Ag Sulfosalts

4.2.1. Diaphorite Ag₃Pb₂Sb₃S₈

Diaphorite is a frequently occurring mineral in studied material (200 point analyses). It was found as anhedral grains up to 150–200 µm in size, most often associated with galena, freieslebenite, boulangerite, freibergite, jamesonite and andorite group minerals in black ore (i) (Figure 2a–e). In the general succession that follows the trend from Pb-rich phases to Ag-rich phases, it is usually a later mineral than freieslebenite and is replaced by freibergite or miargyrite. Macroscopically, visible to naked eye, diaphorite forms lead to steel grey striated crystals up to 3 mm in quartz cavities (occasionally tarnishing black or bronze) and grain aggregates several mm in size in quartz gangue of ore (iii) (Figure 2f) or kutnohorite–quartz gangue of red ore (ii).

The chemical composition of diaphorite from the Anthony of Padua mine (Table 1) shows a considerable variation in Ag/Pb ratio in the range 1.47–1.80. Mozgova et al. [37] described the compositional variation in diaphorite on the basis of microanalytical and crystal structure data from various diaphorite occurrences. They speculated on a continuous solid solution series between diaphorite and a phase with the formula Ag₂PbSb₂S₅ (old unvalid name “brongniardite”) and considered that this phase with Ag/Pb ratios between 1.75 and 2.00 may be an Ag-rich diaphorite. This argument would be supported by the study of diaphorite from Herja (Ag/Pb 1.53–1.69), Rumania [38] or Apuan Alps (Ag/Pb 1.67), Italy [39]. On the other hand, the published data for diaphorite from Kutná Hora [12,35] or Příbram [40] show compositions close to ideal stoichiometry (Ag/Pb 1.44–1.54). The detected range of SSe⁻¹ substitution is limited to 0.29 apfu Se (1.71 wt.%). The maximum contents of Se were found in samples with Ag/Pb ratio about 1.6. Traces of As were also determined.

4.2.2. Freieslebenite AgPbSbS₃

Freieslebenite is fairly common in the studied assemblage (200 point analyses), it occurs as anhedral grains up to 60 × 100 µm in size in black ore (i) in association with boulangerite, owyheeite, galena, diaphorite and miargyrite. Freieslebenite is a later mineral than galena and it is replaced by later diaphorite, miargyrite and minerals of the tetrahedrite groups (Figure 2a–c). Macroscopically, freieslebenite was found as striated steel grey or black metallic crystals up to 2 mm in quartz cavities or grain aggregates in ore (iii).
Figure 2. (a) Black ore (i) association (from the earliest to the latest mineral): galena (Gn), boulangerite (Bou), freieslebenite (Frs), diaphorite (Dia), pyrargyrite (Prg); (b) example of black ore (i) association with the general succession from the Pb-richest to Pb-poorer phases: galena (Gn) – boulangerite (Bou) – freieslebenite (Frs) – owyheeite (Ow) – fizélyite (Fiz) – Ag-excess fizélyite (Aef) – diaphorite (Dia); (c) a later-stage replacement of galena of black ore (i) by Ag-richer minerals following the succession: galena (white) – freieslebenite (Frs) – diaphorite (Dia) – freibergite (Frg) – miargyrite (Mia) – jamesonite (Jms); (d) needles of owyheeite (Ow) replaced by diaphorite (Dia) and Ag-excess fizélyite (Aef); all minerals are subsequently being replaced by miargyrite (Mia); (e) five Ag-minerals in one image: galena (Gn) replaced by freislebenite (Frs), diaphorite (Dia) and Ag-excess fizélyite (Aef), all replaced by miargyrite (Mia). Stephanite (Ste) is the latest mineral. (f) typical example of ore (iii) with prevailing miargyrite (Mia) in quartz gangue, remnants of galena (white) are replaced by diaphorite (Dia) which is subsequently replaced by miargyrite, locally with pyrargyrite inclusions (Prg); freibergite (Frg) is also present. All back-scattered electron images.
Table 1. EPMA data for diaphorite.

| Analyses | wt.% | apfu Σ16 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Sb  | As  | Se  | S   | Total | Ag   | Pb  | Sb  | As  | Se  | S   |
| 477      | 24.21| 29.15| 26.95| 0.05| 0.27| 18.86| 99.48| 3.04| 1.91| 3.00| 0.01| 0.05| 7.97|
| 1107     | 23.63| 28.95| 27.22| 0.09| 0.42| 18.73| 99.03| 2.98| 1.90| 3.05| 0.02| 0.07| 7.96|
| 1106     | 23.96| 28.74| 27.60| 0.03| 0.45| 18.55| 99.33| 3.03| 1.89| 3.09| 0.01| 0.08| 7.89|
| 1733     | 23.84| 28.99| 27.36| 0.18| 0.46| 18.49| 99.32| 3.02| 1.91| 3.07| 0.03| 0.09| 7.93|
| 1850     | 23.43| 29.41| 27.34| 0.18| 0.46| 18.49| 99.32| 3.02| 1.91| 3.07| 0.03| 0.09| 7.93|
| 727      | 24.01| 28.87| 27.02| 0.10| 0.56| 18.82| 99.38| 3.01| 1.89| 3.01| 0.02| 0.10| 7.95|
| 1160     | 24.23| 29.38| 27.55| 0.17| 0.65| 18.73| 99.03| 2.98| 1.90| 3.05| 0.02| 0.07| 7.96|
| 1223     | 24.31| 28.52| 27.23| 0.09| 0.99| 18.47| 99.61| 3.05| 1.86| 3.03| 0.02| 0.17| 7.80|
| 2116     | 23.53| 29.30| 27.21| 0.00| 1.08| 18.37| 100.14| 1.01| 0.97| 1.01| 0.00| 0.19| 7.83|
| 1886     | 24.24| 29.53| 27.49| 0.00| 1.29| 18.71| 101.25| 3.01| 1.91| 3.02| 0.01| 0.22| 7.82|
| 799      | 24.08| 29.20| 27.61| 0.06| 1.64| 18.37| 100.97| 3.01| 1.90| 3.06| 0.01| 0.28| 7.72|
| 800      | 24.42| 29.31| 27.83| 0.05| 1.71| 18.84| 101.76| 3.03| 1.89| 3.06| 0.01| 0.29| 7.69|

Analyses are ordered according to increasing Se content.

Chemical composition of freieslebenite is relatively uniform and close to ideal formula (Table 2); traces of As were identified. The anion part features contents of Se (up to 0.05 apfu, i.e., 0.71 wt.%). The SeS\(^{-1}\) substitution in freieslebenite is the least pronounced of all Ag-Pb-Sb sulfosalts, the maximum determined contents of Se are only 0.71 wt.% compared to 1.71 wt.% in diaphorite and 4.69 wt.% in Ag-excess fizélyite. The empirical formula for studied freieslebenite on the basis of 6 apfu (mean of 138 analyses) can be expressed as Ag\(^{0.99}\)(Pb\(^{0.98}\)Fe\(^{0.01}\))\(^{0.99}\)Sb\(^{1.02}\)(S\(^{2.97}\)Se\(^{0.02}\))\(^{2.99}\).

Table 2. EPMA data for freieslebenite.

| Analyses | wt.% | apfu Σ6 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Sb  | As  | Se  | S   | Total | Ag   | Pb  | Sb  | As  | Se  | S   |
| 569      | 20.50| 37.96| 23.61| 0.08| 0.28| 18.39| 100.82| 0.99| 0.96| 1.01| 0.01| 0.02| 3.00|
| 1737     | 20.17| 38.44| 23.19| 0.13| 0.38| 17.99| 100.30| 0.99| 0.98| 1.02| 0.01| 0.03| 2.97|
| 1861     | 20.14| 38.57| 23.33| 0.15| 0.40| 18.21| 100.80| 0.98| 0.98| 1.02| 0.01| 0.03| 2.99|
| 1205     | 20.18| 38.14| 23.31| 0.09| 0.41| 17.91| 100.03| 0.99| 0.98| 1.02| 0.01| 0.03| 2.97|
| 610      | 20.59| 37.90| 23.27| 0.06| 0.42| 17.90| 100.14| 1.01| 0.97| 1.01| 0.00| 0.03| 2.96|
| 429      | 20.37| 38.21| 23.06| 0.12| 0.44| 18.03| 100.24| 1.00| 0.97| 1.00| 0.01| 0.03| 2.97|
| 713      | 20.37| 38.41| 23.14| 0.06| 0.45| 17.98| 100.41| 1.00| 0.98| 1.01| 0.00| 0.03| 2.96|
| 430      | 20.50| 37.94| 22.89| 0.16| 0.55| 17.89| 99.93| 1.01| 0.97| 1.01| 0.00| 0.04| 2.96|
| 2149     | 20.13| 37.90| 23.15| 0.00| 0.66| 17.83| 99.67| 0.99| 0.97| 1.01| 0.00| 0.04| 2.96|
| 2152     | 20.33| 37.75| 22.89| 0.00| 0.71| 17.49| 99.17| 1.01| 0.98| 1.01| 0.00| 0.05| 2.93|

Analyses are ordered according to increasing Se content.

4.2.3. Ag-excess fizélyite Ag\(_6\)Pb\(_{14}\)Sb\(_{21}\)S\(_{48}\)

Ag-excess fizélyite (AEF) is by far the most abundant of all andorite minerals (ca. 770 analytical points compared to ca. 100 points of all other andorite minerals put together—Figure 3). It is fairly frequent among microprobe analyses in polished sections. It occurs as anhedral grains, occasionally as semi-euhedral or column-like aggregates, usually up to 100 \(\mu\)m, in exceptional cases up to 1500 \(\mu\)m (Figure 4), in black ore (i), most frequently associated with galena, boulangerite, jamesonite, owyheeite, other andorite group minerals and miargyrite (Figure 2b,d,e, Figure 5a–d). AEF usually replaces andorite IV, itself being replaced by freibergite and miargyrite.
Figure 3. Graph $N_{\text{chem}}$ value vs% and substitution (L%) for andorite group minerals.

Figure 4. An exceptionally large grain of Se-rich Ag-excess fizélyite (Aef), 1500 µm across, with a variable Se content (0.31–1.23 wt.% of Se). Ag-excess fizélyite replaces earliest galena (Gn) and is replaced by freieslebenite (Frs).
Figure 5. (a) Andorite IV (Ad4) replaces Ag-excess fízelyite (Aef); (b) grain of Ag-excess fízelyite (Aef) in kutnohorite of black ore (i) is replaced by andorite IV (Ad4), which is subsequently replaced by andorite VI (Ad6; ragged edges). Ag-excess fízelyite is further replaced by freieslebenite (Frs; right side of the grain); (c) galena (Gn) replaced by boulangerite (Bou) and owyheeite (Ow), both minerals subsequently replaced by Ag-excess fízelyite (Aef); (d) earliest galena (Gn) replaced by owyheeite (Ow), Ag-excess fízelyite (Aef) and diaphorite (Dia). All back-scattered electron images.

Ag-excess fízelyite was described for the first time on the basis of chemical analyses as “minéral F” from Les Farges (France) by Moëlo et al. [41] and later from the Lill mine in Příbram (Czech Republic) by Plášil et al. [42]. Structurally, it was defined by Yang et al. [43] in samples from Van Silver mine, Canada. It significantly differs from fízelyite in its higher Ag content. The excess silver is situated at the Ag2 site in the structure [43], which remains unoccupied in “normal” fízelyite. Higher Ag contents result in a shift of calculated N_{chem} (the width of the blocks of octahedra separated by Pb atoms in trigonal prismatic coordination) to higher values above 4. The mineral from Van Silver mine [43] shows calculated values of N_{chem} in the range of 4.31–4.59, mean 4.42. AEF from the Anthony of Padua Mine (Table 3) shows a wider range of N_{chem} values of 4.27–4.91, mean 4.54 (Figure 4). The determined range of the andorite substitution (Ag + Sb = 2Pb) varies between 57.6 and 67.4% (mean 63.7). Apart from sulphur, the anion contains significant selenium content up to 4.48 apfu (4.69 wt.%) (Figure 6), which is considerably higher than in all other andorite group minerals. The empirical formula for studied Ag-excess fízelyite on the basis of 88 apfu (mean of 767 analyses) can be expressed as (Ag_{5.93}Cu_{0.03})_{25.94}(Pb_{13.91}Fe_{0.13}Mn_{0.06})_{21.12}(Sb_{0.57}As_{0.07})_{20.64}(S_{47.68}Se_{0.53})_{24.82}.1
4.2.4. Fizélyite Ag₅Pb₁₄Sb₂₁S₄₈

Fizélyite occurs only rarely in polished section (determined in only seven samples) as euhedral grains of tabular shape with hypoparallel intergrowth. It occurs as inclusions of up to 50 μm in jamesonite enclosed in boulangerite which replaces galena. It also occurs as individual grains in quartz up to 100 μm associated with jamesonite and miargyrite. It is also associated with owyheeite, boulangerite, other andorite minerals and diaphorite (Figure 2a). It is found only in black ore (i), as with all andorite group minerals.

The classification of fizélyite and Ag-excess fizélyite comes from the following assumptions. The formula of fizélyite is Ag₅Pb₁₄Sb₂₁S₄₈, which gives N = 4.00 and L% = 62.49. The formula of Ag-excess fizélyite is Ag₆Pb₁₄Sb₂₁S₄₈, which corresponds to N = 4.46 and L% = 64.85. Considering that AEF defines one more Ag atom compared to fizélyite [43], the borderline between fizélyite and Ag-excess fizélyite must be guided by the content of 0.5 Ag atom more against fizélyite, i.e., by the formula Ag₅.₅Pb₁₄Sb₂₁S₄₈, which yields the values of N = 4.22 and L% = 63.76.

Chemical composition of fizélyite and corresponding chemical formulae are given in Table 4. In comparison with Ag-excess fizélyite (Figure 3), the determined range of Nchem values is centred around an ideal N value equal to 4 and ranges from 3.90 to 4.19 (mean 4.09). Determined values of the Ag + Sb = 2Pb substitution between 57.7 and 62.2% are slightly lower than 62.5 published for ideal fizélyite [41,43]. Found contents of Se do not exceed 1.17 apfu (1.20 wt.%) (Figure 6) and are significantly lower than those found in Ag-excess fizélyite. Another difference against AEF is the presence of minor elements, namely iron. All fizélyite analyses show increased Fe between 0.38 and 0.94 wt.%, mean 0.59, while the same value for AEF is 0.20. The empirical formula for studied fizélyite on the basis of 88 apfu (mean of 9 analyses) can be expressed as

\[(\text{Ag}_4.83\text{Cu}_{0.02})\Sigma4.85(\text{Pb}_{13.58}\text{Fe}_{0.83}\text{Mn}_{0.06}\text{Cd}_{0.03})\Sigma14.50(\text{Sb}_{20.61}\text{As}_{0.04})\Sigma20.65(\text{S}_{47.53}\text{Se}_{0.40})\Sigma47.93\]
Table 3. EPMA data for Ag-excess fizélyite.

| Analyses | wt.% | apfu Σ88 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Fe  | Cd  | Mn  | Sb  | Se  | S   | Total | Ag | Pb  | Fe  | Cd  | Mn  | Sb  | Se  | S   | N   | L%  |
| 1868     | 7.86 | 37.19 | 0.49 | 0.00 | 0.12 | 33.51 | 0.06 | 20.70 | 100.12 | 5.39 | 0.65 | 0.00 | 0.16 | 20.38 | 0.05 | 47.80 | 4.29 | 62.36 |
| 1496     | 8.63 | 37.28 | 0.10 | 0.00 | 0.05 | 33.12 | 0.28 | 20.22 | 99.86 | 6.01 | 0.13 | 0.00 | 0.07 | 20.43 | 0.27 | 47.35 | 4.50 | 65.88 |
| 767      | 8.37 | 37.46 | 0.14 | 0.21 | 0.05 | 32.74 | 0.35 | 20.24 | 99.67 | 5.82 | 0.19 | 0.14 | 0.06 | 20.16 | 0.33 | 47.34 | 4.58 | 62.68 |
| 1392     | 7.84 | 38.31 | 0.13 | 0.00 | 0.20 | 32.23 | 0.46 | 20.07 | 99.36 | 5.50 | 0.17 | 0.00 | 0.27 | 20.03 | 0.44 | 47.35 | 4.54 | 60.74 |
| 1955     | 8.20 | 37.20 | 0.11 | 0.00 | 0.05 | 33.77 | 0.70 | 20.24 | 100.33 | 5.68 | 0.15 | 0.00 | 0.07 | 20.73 | 0.66 | 47.18 | 4.31 | 65.29 |
| 594      | 8.51 | 35.97 | 0.46 | 0.02 | 0.14 | 34.03 | 0.75 | 20.13 | 100.10 | 5.86 | 0.62 | 0.01 | 0.19 | 20.76 | 0.71 | 46.60 | 4.45 | 64.55 |
| 647      | 8.79 | 38.52 | 0.08 | 0.00 | 0.04 | 32.45 | 0.85 | 20.07 | 100.86 | 6.10 | 0.11 | 0.00 | 0.05 | 19.97 | 0.80 | 46.88 | 4.83 | 63.19 |
| 1920     | 7.99 | 37.65 | 0.71 | 0.00 | 0.03 | 32.84 | 0.96 | 19.79 | 100.03 | 5.57 | 0.95 | 0.00 | 0.05 | 20.29 | 0.91 | 46.43 | 4.50 | 60.53 |
| 781      | 8.52 | 36.31 | 0.21 | 0.00 | 0.06 | 33.38 | 1.26 | 20.01 | 99.84 | 5.91 | 0.29 | 0.00 | 0.09 | 20.52 | 1.19 | 46.71 | 4.49 | 65.84 |
| 641      | 8.29 | 37.58 | 0.11 | 0.00 | 0.04 | 32.86 | 1.66 | 19.65 | 100.19 | 5.80 | 0.14 | 0.00 | 0.06 | 20.39 | 1.59 | 46.29 | 4.50 | 63.74 |
| 783      | 8.86 | 36.07 | 0.19 | 0.00 | 0.05 | 33.39 | 1.87 | 19.70 | 100.33 | 6.14 | 0.25 | 0.00 | 0.07 | 20.51 | 1.77 | 45.95 | 4.63 | 67.05 |
| 784      | 8.76 | 36.52 | 0.11 | 0.00 | 0.05 | 33.03 | 2.05 | 19.57 | 100.31 | 6.09 | 0.15 | 0.00 | 0.07 | 20.37 | 1.95 | 45.82 | 4.70 | 66.34 |
| 1148     | 8.71 | 36.68 | 0.05 | 0.00 | 0.02 | 31.99 | 2.86 | 19.14 | 99.47 | 6.14 | 0.06 | 0.00 | 0.03 | 19.99 | 2.75 | 45.42 | 4.73 | 64.83 |
| 1144     | 8.72 | 36.93 | 0.02 | 0.00 | 0.00 | 32.71 | 3.50 | 18.84 | 100.75 | 6.13 | 0.03 | 0.00 | 0.00 | 20.35 | 3.36 | 44.51 | 4.64 | 65.70 |
| 1145     | 8.82 | 36.93 | 0.03 | 0.00 | 0.00 | 32.61 | 3.49 | 18.63 | 100.53 | 6.23 | 0.03 | 0.00 | 0.00 | 20.41 | 3.37 | 44.27 | 4.70 | 65.69 |
| 1143     | 9.07 | 37.30 | 0.02 | 0.00 | 0.01 | 33.11 | 4.69 | 18.63 | 102.91 | 6.28 | 0.03 | 0.00 | 0.01 | 20.29 | 4.43 | 43.34 | 4.73 | 65.98 |

Analyses are ordered according to increasing Se content.

Table 4. EPMA data for fizélyite.

| Analyses | wt.% | apfu Σ88 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Fe  | Cd  | Mn  | Sb  | Se  | S   | Total | Ag | Pb  | Fe  | Cd  | Mn  | Sb  | Se  | S   | N   | L%  |
| 556      | 6.90 | 37.65 | 0.65 | 0.36 | 0.07 | 33.84 | 0.21 | 20.84 | 100.57 | 4.72 | 0.86 | 0.24 | 0.09 | 20.49 | 0.20 | 47.91 | 4.05 | 58.51 |
| 479      | 6.98 | 37.56 | 0.53 | 0.04 | 0.07 | 33.30 | 0.23 | 19.93 | 98.62 | 4.93 | 0.72 | 0.02 | 0.10 | 20.83 | 0.23 | 47.32 | 4.08 | 59.54 |
| 1172     | 7.46 | 37.95 | 0.38 | 0.00 | 0.09 | 39.92 | 0.25 | 20.63 | 100.74 | 5.12 | 0.50 | 0.00 | 0.12 | 20.64 | 0.24 | 47.68 | 4.15 | 61.58 |
| 729      | 6.71 | 37.18 | 0.94 | 0.01 | 0.06 | 33.33 | 0.32 | 20.42 | 99.03 | 4.65 | 1.26 | 0.01 | 0.08 | 20.49 | 0.30 | 47.65 | 4.02 | 58.00 |
| 1903     | 7.43 | 37.71 | 0.45 | 0.00 | 0.01 | 34.19 | 0.72 | 20.44 | 101.05 | 5.10 | 0.60 | 0.00 | 0.02 | 20.79 | 0.68 | 47.19 | 4.10 | 62.23 |
| 2062     | 7.11 | 36.56 | 0.57 | 0.00 | 0.03 | 33.33 | 1.20 | 19.25 | 98.06 | 5.07 | 0.79 | 0.00 | 0.04 | 21.07 | 1.17 | 46.22 | 4.06 | 61.44 |

Analyses are ordered according to increasing Se content.
4.2.5. Andorite IV $\text{Ag}_{15}\text{Pb}_{18}\text{Sb}_{47}\text{S}_{86}$

Andorite IV is the second most frequent andorite mineral (10 samples, 70 point analyses). It is most often found as grains and inclusions up to 300 $\mu$m in Ag-excess filélyte which is replaced by andorite IV, and also as worm-like relict aggregates associated with andorite VI, occasionally mutually intergrowing, associated with boulangerite, owyheeite, jamesonite, freieslebenite and diaphorite in black ore (i) (Figure 5a, b). Andorite IV is sometimes as lamellae as much as 150 $\mu$m long and 30 $\mu$m wide. According to the degree of replacement, only amoebic relics, frayed or ragged at the edges, remain. The earliest mineral in the association is galena, followed by andorite IV, which is replaced by andorite VI, which are corroded by owyheeite and fizlyite. Thus, this is an opposite trend to the general succession.

Chemical analyses of andorite IV (Table 5, Figure 3) revealed $N_{\text{chem}}$ values between 3.88 and 4.09 (mean 3.96) and L% (percentage of the andorite 2Pb = Ag + Sb substitution) between 90.21 and 97.21 (mean 94.18), which is in a good agreement with published data of this mineral phase [41]. The SeS$_{-1}$ substitution does not exceed 3.24 apfu (1.76 wt.% Se) (Figure 6).

4.2.6. Andorite VI, $\text{AgPbSb}_3\text{S}_6$

Andorite VI is much less frequent than andorite IV (17 point analyses of four samples). It was found in black ore (i) as anhedral grains up to 80 $\mu$m in earlier Ag-excess filélyte, which is replaced by andorite IV, which is then replaced by andorite VI, and, occasionally, as anhedral grains up to 250 $\mu$m in earlier Ag-excess filélyte with all or most of andorite IV being replaced by andorite VI (Figure 5b). It is the mineral with the highest andorite substitution (2Pb = Ag + Sb), i.e. the lowest Pb and highest Ag and Sb contents, and it appears as the latest mineral in the association of andorite group minerals.

Chemical composition of andorite VI and corresponding chemical formulae are given in Table 6. $N_{\text{chem}}$ values 3.80–4.02 (mean 3.91) and the andorite substitution percentage (L%) 97.4–102.2 (Figure 3) correspond to the published data of this mineral [41]. The Se for S substitution is similar to andorite IV and does not exceed 0.15 apfu (1.31 wt.% (Figure 6).

4.2.7. Owyheeite, $\text{Ag}_3\text{Pb}_{10}\text{Sb}_{11}\text{S}_{28}$

Owyheeite occurs as massive needle-like steel to lead grey aggregates up to 2 cm long in quartz and kutnohorite associated or intergrowing with massive boulangerite, miargyrite and pyrite. It occurs in black ore (i) associated with galena, Pb-Sb sulfosalts (boulangerite, jamesonite) and Ag-Pb-Sb sulfosalts (andorite group minerals, freieslebenite and diaphorite) (Figure 5c, d). It is frequent in polished sections (160 point analyses). It was found as elongated lamellae up to 100 $\mu$m in length and 20 $\mu$m in width forming massive grains several hundred microns across.

The chemical composition of owyheeite (Table 7) is close to ideal formula $\text{Ag}_3\text{Pb}_{10}\text{Sb}_{11}\text{S}_{28}$ proposed by Moëlo et al. [44], with a slight deficit of Pb and an excess of Sb. Figure 7 shows that contents of main elements Ag, Pb and Sb do not correlate significantly and the 2Pb $\square$ Ag + Sb substitution presented by Moëlo et al. [45] is not the dominant factor in the chemical composition of owyheeite. The determined contents of selenium in the studied mineral are relatively low (0.12–1.17 apfu; 0.21–1.97 wt.%). Its average composition (113 analyses) is possible to express by empirical formula $(\text{Ag}_{2.96}\text{Cu}_{0.03})_{1.2}^{+}(\text{Pb}_{9.69}\text{Fe}_{0.02})_{2.96}^{+}(\text{Sb}_{11.18}\text{As}_{0.03})_{11.21}^{+}(\text{S}_2\text{S}_{7.75}\text{Se}_{0.36}\text{Cl}_{0.04})_{1.28}^{+}$ on the basis of 52 apfu.
### Table 5. EPMA data for andorite IV.

| Analyses | wt.% | apfu Σ88 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Fe  | Sb  | As  | Se  | S    | Total | Ag   | Pb  | Fe  | Sb  | As  | Se  | S    | N       | L%  |
| A        |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
| B        |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
| C        |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |         |     |

Analyses are ordered according to increasing Se content.

### Table 6. EPMA data for andorite VI.

| Analyses | wt.% | apfu Σ11 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Fe  | Sb  | As  | Se  | S    | Total | Ag   | Pb  | Fe  | Sb  | As  | Se  | S    | N      | L%   |
| A        |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
| B        |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
| C        |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |
|          |      |     |     |     |     |     |      |       |      |     |     |     |     |     |      |        |      |

Analyses are ordered according to increasing Se content.
Table 7. EPMA data for owyeeite.

| Analyses | wt.% | apfu Σ52 Atoms |
|----------|------|---------------|
|          | Ag   | Pb | Fe | Sb | As | Se | S | Total | Ag | Cu | Pb | Fe | Sb | As | Se | S |
| 822      | 6.70 | 44.08 | 0.09 | 28.90 | 0.00 | 0.21 | 19.34 | 99.32 | 2.88 | 0.03 | 9.86 | 0.08 | 11.00 | 0.03 | 0.12 | 27.95 |
| 1004     | 6.81 | 43.21 | 0.00 | 29.59 | 0.07 | 0.54 | 19.50 | 99.72 | 2.90 | 0.01 | 9.56 | 0.03 | 11.15 | 0.04 | 0.31 | 27.89 |
| 1193     | 6.87 | 43.79 | 0.05 | 29.42 | 0.00 | 1.14 | 19.45 | 100.72 | 2.90 | 0.02 | 9.63 | 0.04 | 11.01 | 0.02 | 0.66 | 27.65 |
| 1190     | 6.92 | 43.69 | 0.11 | 29.51 | 0.00 | 0.93 | 19.36 | 100.51 | 2.93 | 0.03 | 9.64 | 0.09 | 11.09 | 0.01 | 0.54 | 27.61 |
| 1195     | 6.98 | 44.06 | 0.00 | 29.80 | 0.07 | 0.96 | 19.45 | 101.32 | 2.94 | 0.02 | 9.67 | 0.02 | 11.13 | 0.04 | 0.55 | 27.58 |
| 1192     | 6.97 | 43.36 | 0.05 | 29.55 | 0.08 | 1.09 | 19.26 | 100.35 | 2.96 | 0.01 | 9.59 | 0.04 | 11.12 | 0.05 | 0.63 | 27.53 |
| 1191     | 6.98 | 43.51 | 0.00 | 29.50 | 0.06 | 1.04 | 19.30 | 100.38 | 2.96 | 0.01 | 9.62 | 0.03 | 11.10 | 0.04 | 0.60 | 27.58 |
| 1194     | 7.06 | 43.39 | 0.00 | 29.51 | 0.07 | 1.11 | 19.26 | 100.41 | 3.00 | 0.02 | 9.59 | 0.03 | 11.10 | 0.04 | 0.64 | 27.51 |
| 1188     | 7.10 | 43.64 | 0.08 | 29.76 | 0.00 | 0.97 | 19.31 | 100.87 | 3.01 | 0.02 | 9.62 | 0.07 | 11.16 | 0.02 | 0.56 | 27.50 |
| 712      | 7.19 | 43.18 | 0.26 | 29.58 | 0.07 | 0.93 | 19.29 | 100.51 | 3.04 | 0.03 | 9.52 | 0.21 | 11.09 | 0.04 | 0.54 | 27.47 |
| 1511     | 7.14 | 43.05 | 0.00 | 29.52 | 0.12 | 1.09 | 18.95 | 99.86 | 3.06 | 0.03 | 9.60 | 0.02 | 11.20 | 0.07 | 0.64 | 27.31 |
| 1698     | 7.23 | 44.14 | 0.00 | 28.86 | 0.16 | 0.42 | 19.40 | 100.20 | 3.08 | 0.06 | 9.78 | 0.01 | 10.89 | 0.10 | 0.24 | 27.79 |
| 1503     | 7.24 | 42.30 | 0.07 | 29.70 | 0.09 | 0.93 | 19.10 | 99.43 | 3.09 | 0.03 | 9.41 | 0.06 | 11.24 | 0.06 | 0.55 | 27.45 |
| 1512     | 7.24 | 42.51 | 0.00 | 29.69 | 0.19 | 1.63 | 18.79 | 100.03 | 3.10 | 0.01 | 9.47 | 0.00 | 11.26 | 0.12 | 0.95 | 27.05 |
| 2095     | 7.47 | 42.21 | 0.00 | 30.38 | 0.00 | 0.44 | 19.35 | 99.85 | 3.18 | 0.02 | 9.35 | 0.03 | 11.45 | 0.00 | 0.26 | 27.69 |

Analyses are ordered according to increasing Ag content.
oulangerite, miargyrite and pyrite
ctions (160 point analyses). It was found as elongated lamellae up to 100 μm

3

\[ \text{Eq. 1} \]

ag-poor Ag-Pb-Sb sulfosalts, this paper

boulangerite

zoubekite ideal composition AgPb

Jms

Aps

Gn

Jms

Bou

Aei

Gn

Primorye [49]; UM1979

Cl

Ag

Cu

Sb

Fe

As

Pb

Figure 7. Graph Ag + Cu vs Sb + As (apfu) (a) and Ag + Cu vs Pb + Fe (apfu) (b) for owyheeite.

4.2.8. Ag-Poor Ag-Pb-Sb Sulfosalts

Ag-poor Ag-Pb-Sb sulfosalts are chemically similar to owyheeite, but show lower contents of Ag and higher contents of Pb. Most often it forms lamellae several tens of microns across enclosed in owyheeite or boulangerite, which it replaces (in agreement with the general succession) (Figure 8). It is closely associated with owyheeite, boulangerite, galena, jamesonite and Ag-excess fízélyite. It is much rarer than owyheeite (21 point analyses, compared to 160 analyses of owyheeite).

Figure 8. Grain of Ag-poor Ag-Pb-Sb sulfosalt (Aps, 3.3 wt.% Ag) in boulangerite (Bou) in association with jamesonite (Jms), Ag-excess fízélyite (Aei) and galena (Gn). The succession runs as: galena – boulangerite – jamesonite – Ag-poor Ag-Pb-Sb sulfosalt – Ag-excess fízélyite.

The Ag-poor part (with Ag contents lower than in the case of owyheeite) is an interesting and so far not a well-known part of the Ag-Pb-Sb-S system, with only two approved minerals—questionable zoubekite [45,46] and tubulite—with unusual tubular morphology and crystal structure [47]. We identified mineral phases with 0.7–4.3 at.% Ag (0.87–5.12 wt.% Ag), which can be divided into four groups of compositions (Table 8) differing by Ag content: a) four analyses with 0.87–1.16 wt.% of Ag; b) nine analyses with 2.02–2.87 wt.% Ag; c) four analyses with 3.31–4.29 wt.%; and d) four analyses with 5.08–5.20 wt.% The determined Ag and Pb contents show negative correlation with
ratio ca. 1:1 (Figure 9a); a less pronounced positive correlation was found between Ag and Sb with ratio ca. 2:1 (Figure 9b). Both correlations in principle fit the line between zoubekite and boulangerite. The substitution scheme can be expressed as Pb □ Ag + 0.5Sb. The chemical composition of found Ag-poor Ag-Pb-Sb sulfosalts is close to two mineral phases: the recently described mineral tubulite Ag₃Pb₂Sb₂₀S₃₃, which, however, differs in its very unusual and specific tube-like morphology [47]; and an unnamed phase M3 with the ideal formula AgPb₁₁Sb₁₁S₉₀ described by Megerskaja and Rykl [48] from Příbram, Czech Republic. Other unnamed phases in this system differ first of all by having higher Pb contents and lower Sb (Figure 9a,b). The Sb contents found in Ag-poor Ag-Pb-Sb sulfosalts are relatively low, within 0.22–1.54 at.% (0.18–1.35 wt.% Se). The chemical compositions and corresponding formula coefficients calculated for 52 apfu (as in owyheeite) are given in Table 8.

Table 8. EPMA data for Ag-poor Ag-Pb-Sb sulfosalts.

| Analyses     | wt%          | apfu Σ28 Atoms |
|--------------|--------------|----------------|
|              | Ag | Pb | Fe | Sb | As | Se | S  | Total | Cu | Pb | Fe | Sb | As | Se | S  | Total |
| 495          | 0.87 | 49.27 | 1.95 | 27.19 | 0.00 | 0.32 | 19.84 | 99.43 | 0.37 | 0.01 | 10.93 | 1.60 | 10.27 | 0.02 | 0.19 | 28.44 |
| 1513         | 1.05 | 52.45 | 0.09 | 27.14 | 0.10 | 0.95 | 18.81 | 100.59 | 0.46 | 0.01 | 12.01 | 0.08 | 10.58 | 0.06 | 0.57 | 27.83 |
| 1325         | 1.17 | 52.47 | 0.46 | 26.70 | 0.00 | 0.55 | 18.94 | 100.29 | 0.52 | 0.02 | 12.06 | 0.39 | 10.45 | 0.02 | 0.33 | 28.14 |
| 904          | 1.18 | 51.76 | 0.00 | 27.01 | 0.09 | 0.37 | 18.33 | 99.66 | 0.91 | 0.02 | 12.15 | 0.03 | 11.48 | 0.10 | 22.78 |
| 1359         | 2.02 | 51.78 | 0.00 | 28.04 | 0.00 | 0.44 | 18.37 | 99.83 | 0.53 | 0.01 | 12.10 | 0.03 | 11.18 | 0.00 | 27.82 |
| 323          | 2.03 | 50.64 | 0.00 | 27.45 | 0.05 | 0.25 | 18.53 | 98.95 | 0.91 | 0.01 | 11.84 | 0.03 | 10.92 | 0.03 | 16.00 |
| 991          | 2.11 | 50.36 | 0.00 | 27.19 | 0.00 | 0.91 | 18.82 | 99.49 | 0.98 | 0.00 | 11.62 | 0.02 | 10.68 | 0.03 | 55.07 |
| 490          | 2.36 | 47.86 | 0.94 | 28.64 | 0.05 | 0.36 | 19.53 | 99.73 | 1.01 | 0.01 | 10.69 | 0.78 | 10.89 | 0.03 | 21.19 |
| 321          | 2.26 | 48.55 | 0.07 | 27.80 | 0.10 | 0.91 | 18.68 | 97.64 | 1.01 | 0.00 | 11.36 | 0.06 | 11.07 | 0.06 | 21.24 |
| 1502         | 2.48 | 50.13 | 0.12 | 28.26 | 0.10 | 1.35 | 18.87 | 101.30 | 1.08 | 0.00 | 11.32 | 1.00 | 10.86 | 0.06 | 20.73 |
| 580          | 2.71 | 48.99 | 0.06 | 28.36 | 0.00 | 1.70 | 19.12 | 99.95 | 1.19 | 0.00 | 11.15 | 0.05 | 10.98 | 0.02 | 42.11 |
| 2227         | 2.69 | 50.88 | 0.06 | 28.61 | 0.00 | 0.20 | 18.81 | 99.25 | 1.20 | 0.02 | 11.81 | 0.05 | 10.51 | 0.00 | 12.22 |
| 891          | 2.87 | 47.51 | 0.12 | 29.17 | 0.00 | 0.48 | 19.37 | 99.52 | 1.25 | 0.01 | 10.75 | 0.10 | 11.23 | 0.00 | 20.32 |
| 2774         | 3.31 | 47.97 | 0.00 | 27.86 | 0.00 | 0.27 | 18.82 | 98.23 | 1.47 | 0.06 | 11.11 | 0.01 | 10.98 | 0.02 | 17.17 |
| 2775         | 3.53 | 47.84 | 0.00 | 28.02 | 0.07 | 0.29 | 18.66 | 98.41 | 1.57 | 0.08 | 11.09 | 0.00 | 11.05 | 0.05 | 18.75 |
| 578          | 3.92 | 46.80 | 0.00 | 29.39 | 0.05 | 0.42 | 18.77 | 99.34 | 1.72 | 0.01 | 10.71 | 0.04 | 11.44 | 0.03 | 25.75 |
| 895          | 4.29 | 45.97 | 0.00 | 28.46 | 0.00 | 0.51 | 18.90 | 98.12 | 1.89 | 0.02 | 10.55 | 0.02 | 11.12 | 0.01 | 31.04 |
| 1003         | 5.08 | 44.78 | 0.00 | 28.62 | 0.06 | 0.52 | 19.22 | 98.27 | 2.21 | 0.03 | 10.14 | 0.03 | 11.03 | 0.03 | 31.13 |
| 992          | 5.12 | 43.91 | 0.06 | 30.87 | 0.06 | 0.89 | 19.28 | 100.18 | 2.18 | 0.05 | 9.76 | 0.05 | 11.67 | 0.04 | 52.69 |
| 1389         | 5.16 | 43.81 | 0.09 | 30.23 | 0.00 | 0.39 | 20.05 | 99.82 | 2.18 | 0.00 | 9.63 | 0.07 | 11.34 | 0.02 | 22.47 |
| 909          | 5.20 | 44.51 | 0.00 | 28.46 | 0.00 | 0.55 | 18.90 | 97.62 | 2.29 | 0.01 | 10.20 | 0.01 | 11.09 | 0.02 | 33.78 |

Analyses are ordered according to increasing Ag content.

Figure 9. (a) Graph Ag + Cu vs Pb + Fe (at.%) for Ag-poor Ag-Pb-Sb sulfosalts and owyheeite; boulangerite ideal composition Pb₂Sb₁₁S₉₀; T-tubulite ideal composition Ag₃Pb₂Sb₂₀S₃₃ [47]; unnamed M3—Příbram [48]; unnamed M2—Příbram [48]; UM1979-14—Primorye [49,50]; UM1990-32—Příbram; zoubekite ideal composition AgPb₄Sb₄S₁₀ [46]. (b) graph Ag + Cu vs. Sb + As (at.%) for Ag-poor Ag-Pb-Sb sulfosalts and owyheeite; boulangerite ideal composition Pb₂Sb₁₁S₉₀; T-tubulite ideal composition Ag₃Pb₂Sb₂₀S₃₃ [47]; unnamed M3—Příbram [48]; unnamed M2—Příbram [48]; UM1979-14—Primorye [49]; UM1990-32—Příbram; zoubekite ideal composition AgPb₄Sb₄S₁₀ [46].
4.3. Pb-Sb Sulfosalts

4.3.1. Boulangerite, Pb$_5$Sb$_4$S$_{11}$

Boulangerite occurs as abundant lead grey felt-like aggregates and needle crystals in quartz cavities up to 1 cm or as massive grain needle-like aggregates several cm in size associated with galena and miargyrite in black ore type (i). In polished sections (170 point analyses), it occurs as needle-like and column-like crystals up to 80 µm in length and 10 µm in width associated with galena, freislebenite, jamesonite, andorite group minerals and pyrite (Figure 2a,b, Figure 5c, Figure 8, Figure 10a,b) of black ore (i). Also occurs as lenses in white quartz of ore (iii) consisting of massive fibrous and needle-like grains associated with jamesonite and galena. It belongs to the earliest minerals in the observed mineral associations, next to galena.

The chemical composition of boulangerite (Table 9) is close to ideal stoichiometry; only traces of Fe, Mn and Ag were identified. In anion, contents of Se up to 0.63 apfu (2.69 wt.%) (Figure 11) were observed, which is significantly more than in other Pb-Sb sulfosalts (jamesonite, semseyite). Its average composition (167 analyses) is possible to express by the empirical formula (Pb$_{4.89}$Fe$_{0.01}$Mn$_{0.01}$)$_2$Sb$_{4.03}$S$_{10.89}$Se$_{0.12}$Sms$_{11.01}$ on the basis of 20 apfu.

Table 9. EPMA data for boulangerite.

| Analyses | wt.% | apfu Σ20 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Fe  | Mn  | Sb  | As  | Se  | S    | Total | Ag | Pb | Fe | Mn | Sb | As | Se | S | Total |
| 2468     | 0.00 | 55.00 | 0.16 | 0.15 | 25.47 | 0.00 | 0.00 | 18.50 | 99.28 | 0.00 | 5.02 | 0.05 | 0.05 | 3.96 | 0.00 | 0.00 | 0.00 | 10.91 |
| 2475     | 0.00 | 54.56 | 0.00 | 0.06 | 26.35 | 0.00 | 0.04 | 18.89 | 99.90 | 0.00 | 4.92 | 0.01 | 0.02 | 4.04 | 0.00 | 0.01 | 0.00 | 11.00 |
| 2226     | 0.25 | 54.29 | 0.11 | 0.06 | 26.35 | 0.00 | 0.09 | 18.71 | 99.86 | 0.00 | 4.90 | 0.02 | 0.02 | 4.05 | 0.00 | 0.02 | 0.00 | 10.92 |
| 368      | 0.00 | 54.52 | 0.00 | 0.00 | 26.17 | 0.09 | 0.24 | 18.74 | 99.76 | 0.01 | 4.92 | 0.00 | 0.01 | 4.02 | 0.02 | 0.06 | 0.00 | 10.93 |
| 1644     | 0.12 | 55.08 | 0.00 | 0.00 | 25.10 | 0.10 | 0.31 | 18.54 | 99.24 | 0.02 | 5.03 | 0.00 | 0.01 | 3.90 | 0.02 | 0.07 | 0.00 | 10.94 |
| 1855     | 0.00 | 54.74 | 0.00 | 0.00 | 26.35 | 0.08 | 0.59 | 18.64 | 100.39 | 0.00 | 4.93 | 0.00 | 0.00 | 4.04 | 0.02 | 0.14 | 0.00 | 10.85 |
| 1940     | 0.00 | 54.80 | 0.00 | 0.05 | 26.81 | 0.05 | 0.61 | 18.90 | 101.21 | 0.00 | 4.88 | 0.01 | 0.02 | 4.06 | 0.01 | 0.14 | 0.00 | 10.87 |
| 718      | 0.05 | 53.97 | 0.00 | 0.00 | 26.04 | 0.00 | 0.85 | 18.73 | 99.64 | 0.01 | 4.86 | 0.01 | 0.01 | 3.99 | 0.01 | 0.20 | 0.00 | 10.90 |
| 581      | 0.00 | 55.21 | 0.00 | 0.00 | 26.12 | 0.00 | 1.07 | 18.59 | 101.00 | 0.00 | 4.95 | 0.00 | 0.01 | 3.99 | 0.01 | 0.25 | 0.00 | 10.78 |
| 757      | 0.00 | 54.13 | 0.17 | 0.00 | 25.62 | 0.00 | 1.93 | 18.25 | 100.09 | 0.00 | 4.89 | 0.06 | 0.01 | 3.93 | 0.00 | 0.46 | 0.00 | 10.64 |
| 1515     | 0.00 | 54.01 | 0.10 | 0.09 | 26.29 | 0.06 | 2.21 | 18.07 | 100.84 | 0.00 | 4.85 | 0.03 | 0.03 | 4.01 | 0.02 | 0.52 | 0.00 | 10.48 |
| 748      | 0.00 | 54.29 | 0.06 | 0.00 | 26.17 | 0.00 | 2.69 | 18.12 | 101.30 | 0.01 | 4.86 | 0.02 | 0.01 | 3.99 | 0.00 | 0.63 | 0.00 | 10.48 |

Analyses are ordered according to increasing Se content.
4.3. Semseyite, Pb₅Sb₆S₂₁

Semseyite was found in a similar association as boulangerite, but is much rarer, it usually occurs as needle-like or tabular grain up to 20 µm in length and 15 µm in width (Figure 10b). The chemical composition of semseyite (Table 10) corresponds to ideal stoichiometry of this mineral phase; Ag content in one point analysis (0.19 apfu) can be influenced by the surrounding phases. Unlike other Pb-Sb sulfosalts, semseyite is virtually Se-free (Figure 11). Its empirical formula (mean of 4 analyses) is (Pb₈.₉₁Ag₀.₀₅)S₈.₉₆Sb₇.₉₅S₂₁.₀₈ on the basis of 38 apfu.

Table 10. EPMA data for semseyite.

| Analyses | wt.% | apfu Σ38 Atoms |
|----------|------|----------------|
|          | Ag   | Pb  | Sb  | S   | Total | Ag   | Pb  | Sb  | S   |
| 2462     | 0.00 | 52.82 | 27.46 | 19.53 | 99.92 | 0.00 | 8.89 | 7.87 | 21.24 |
| 2482     | 0.57 | 50.70 | 27.18 | 19.18 | 97.63 | 0.19 | 8.68 | 7.92 | 21.22 |
| 2483     | 0.00 | 52.41 | 27.04 | 18.81 | 98.42 | 0.00 | 9.05 | 7.95 | 21.00 |
| 2463     | 0.00 | 52.71 | 27.72 | 18.85 | 99.46 | 0.00 | 9.02 | 8.07 | 20.84 |

4.3.3. Jamesonite, Pb₄FeSb₆S₁₄

Jamesonite occurs as needle crystals in quartz gangue or as massive grain needle-like aggregates up to 2 cm in black ore (i) and ore (iii). In the polished section, it was found as long needles up to 150 µm in length and 20 µm in width. It usually replaces galena and grows together with boulangerite, freibergite and pyrite (Figure 2c, Figure 8). It belongs to the earliest minerals in the association.

The chemical composition of jamesonite (100 point analyses) is relatively uniform (Table 11) and close to ideal formula; only minor contents of Mn (up to 0.11 apfu) and Se (up to 0.27 apfu) were identified (Figure 11). The observed range of SeS₁ substitution is distinctly lower than in boulangerite (Figure 11). The empirical formula for studied jamesonite on the basis of 25 apfu (mean of 84 analyses) can be expressed as Fe₀.₉₅Mn₀.₀₂Pb₃₉₇Sb₆.₀₅(S₁₃.₉₄Se₀.₀₇)₂₁₄.₀₁.
Table 11. EPMA data for jamesonite.

| Analyses | wt.%     | \( \text{apfu} \ \Sigma 20 \) Atoms |
|----------|----------|--------------------------------------|
|          | Pb  | Fe  | Mn  | Sb | Se | S   | Total | Pb  | Fe  | Mn  | Sb | Se | S   |
| 2450     | 39.14| 2.35| 0.09| 34.95| 0.00| 21.77 | 98.50 | 3.92 | 0.95 | 0.03 | 5.96 | 0.00 | 14.10 |
| 379      | 40.51| 2.56| 0.00| 35.12| 0.09| 21.90 | 100.17 | 4.02 | 0.94 | 0.02 | 5.93 | 0.02 | 14.03 |
| 213      | 39.67| 2.61| 0.00| 35.80| 0.30| 21.22 | 99.60 | 3.99 | 0.98 | 0.01 | 6.13 | 0.08 | 13.80 |
| 864      | 39.45| 2.47| 0.06| 35.44| 0.41| 21.70 | 99.53 | 3.93 | 0.91 | 0.02 | 6.01 | 0.11 | 13.98 |
| 1304     | 39.29| 2.62| 0.10| 35.76| 0.43| 21.91 | 100.09 | 3.88 | 0.96 | 0.04 | 6.01 | 0.11 | 13.99 |
| 863      | 39.69| 2.41| 0.10| 36.12| 0.44| 21.74 | 100.49 | 3.93 | 0.89 | 0.04 | 6.08 | 0.11 | 13.90 |
| 1906     | 39.24| 2.51| 0.05| 36.05| 0.61| 21.88 | 100.34 | 3.87 | 0.92 | 0.02 | 6.06 | 0.16 | 13.96 |
| 2069     | 38.48| 2.45| 0.14| 35.56| 0.83| 20.81 | 98.27 | 3.92 | 0.93 | 0.05 | 6.16 | 0.22 | 13.70 |

Analyses are ordered according to increasing Se content.

4.4. Ag-Sb Sulfsalts

4.4.1. Miargyrite, AgSbS₂

Miargyrite is by far the most abundant silver mineral in the Kutná Hora ore district, together with freibergite. Short column-like grey-black crystals of miargyrite up to 10 mm in size in cavities of milky quartz gangue (ore (iii)), or quartz–kutnohorite gangue (ore (ii)) are famous from this locality [36]. Frequently, miargyrite forms massive grain aggregates and lenses in all three types of ore of several centimetres in size, often intergrowing with other Ag minerals such as pyrargyrite, diaphorite, freibergite and freieslebenite. In polished sections, it was found as groups of anhedral grains several hundred \( \mu \text{m} \) in size and occasional euhedral crystals into cavities. It appears in two generations at least, the latter being characteristic of a considerably smaller size of grains (up to 20 \( \mu \text{m} \)), higher selenium content (Figure 12a) and the association of members of galena – claustralite solid solution. The two generations appear in all three of the above-mentioned ores (i, ii and iii), examples of miargyrite in black ore (i) are in Figures 2c–e and 12a; red ore (ii) in Figure 12b and ore (iii) in Figure 2f.

![Figure 12](a) (a) Galena (Gn)—the earliest mineral in the association—is replaced by diaphorite (Dia), which is subsequently replaced by Ag-excess fizélyite (Aef). Both minerals are replaced by miargyrite (Mia), whereas miargyrite with 1 wt.% Se (darker) is replaced by the second-generation Se-rich miargyrite (lighter, 5% Se). (b) miargyrite (Mia) embedded in sphalerite (Sp). An argyrodite (Agd) inclusion is on the boundary between sphalerite and pyrite (Py), both minerals (miargyrite and argyrodite) replace sphalerite. Both back-scattered electron (BSE) images.

Chemical analyses of miargyrite (175 points) revealed interesting Se contents (Figure 13a,b), otherwise it is close to the ideal formula. Determined traces of Pb, Cu and Fe in some of analyses
are probably caused by microscopic intergrowths with other phases; irregular contents of As do not exceed 0.01 apfu (0.19 wt.%). The prevailing earlier generation of miargyrite contains up to 0.08 apfu (2.29 wt.%) of Se; the later generation of miargyrite shows a considerably larger extent of the Se$_{\text{S-1}}$ substitution, usually between 0.11 and 0.35 apfu, corresponding to the maximum Se content of 8.79 wt.%. Two exceptionally high Se contents were measured in small anhedral grains of miargyrite in sphalerite of red ore (ii), belonging to the later generation. These show 0.57 and 0.62 apfu—not included in Table 12 due to increased Zn content from neighbouring sphalerite. The more significant contents of Se in miargyrite were so far described only by Nekrasov, Lunin [51] and Yunfen et al. [52]. The representative chemical analyses of both miargyrite generation and corresponding empirical formulae are given in Table 12.

![Graph](image)

**Figure 13.** (a) Graph S vs Se (apfu) for two types of miargyrite. (b) graph Se/(S + Se) vs Ag (at.%) for Ag-Sb-S mineral phases.

| Analyses | wt.% | apfu Z4 Atoms |
|----------|------|---------------|
| Ag | Pb | Fe | Sb | As | Se | S | Total | Ag | Cu | Pb | Fe | Cd | Sb | As | Se | S |
| 514 | 37.18 | 0.00 | 0.00 | 41.06 | 0.17 | 0.00 | 21.83 | 100.23 | 1.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.99 | 0.01 | 0.00 | 1.99 |
| 52 | 36.32 | 0.10 | 0.06 | 41.47 | 0.08 | 0.33 | 21.47 | 99.83 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 1.01 | 0.00 | 0.01 | 1.98 |
| 57 | 35.95 | 0.23 | 0.07 | 40.80 | 0.13 | 0.51 | 21.65 | 99.34 | 0.98 | 0.00 | 0.00 | 0.00 | 0.00 | 0.99 | 0.01 | 0.02 | 1.99 |
| 58 | 35.99 | 0.34 | 0.08 | 41.10 | 0.10 | 0.69 | 21.32 | 99.62 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.00 | 0.03 | 1.97 |
| 8 | 36.35 | 0.10 | 0.00 | 41.74 | 0.08 | 0.88 | 21.36 | 100.51 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 1.01 | 0.00 | 0.01 | 1.98 |
| 1963 | 36.13 | 0.06 | 0.00 | 41.81 | 0.07 | 1.08 | 21.05 | 100.18 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 1.02 | 0.00 | 0.04 | 1.94 |
| 791 | 35.67 | 0.20 | 0.06 | 40.68 | 0.10 | 1.76 | 20.70 | 99.16 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.00 | 0.07 | 1.93 |
| 539 | 36.42 | 0.08 | 0.00 | 41.05 | 0.07 | 3.46 | 20.09 | 101.18 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.00 | 0.13 | 1.86 |
| 1137 | 35.57 | 0.09 | 0.00 | 40.44 | 0.00 | 4.26 | 19.13 | 99.50 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.01 | 0.00 | 0.16 | 1.82 |
| 1362 | 35.16 | 0.06 | 0.16 | 40.10 | 0.05 | 4.92 | 19.53 | 99.99 | 0.98 | 0.00 | 0.00 | 0.01 | 0.00 | 0.99 | 0.00 | 0.19 | 1.83 |
| 1138 | 34.97 | 0.40 | 0.00 | 40.01 | 0.00 | 5.63 | 18.40 | 99.40 | 1.00 | 0.00 | 0.01 | 0.00 | 0.00 | 1.01 | 0.00 | 0.22 | 1.76 |
| 1265 | 35.18 | 0.21 | 0.08 | 40.05 | 0.06 | 6.35 | 18.19 | 100.12 | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.01 | 0.00 | 0.25 | 1.74 |
| 2699 | 35.18 | 0.08 | 0.46 | 39.06 | 0.00 | 8.65 | 16.85 | 100.27 | 1.01 | 0.00 | 0.00 | 0.03 | 0.00 | 0.99 | 0.00 | 0.34 | 1.63 |
| 2700 | 34.83 | 0.06 | 0.40 | 38.93 | 0.00 | 8.79 | 16.34 | 99.34 | 1.01 | 0.00 | 0.00 | 0.02 | 0.00 | 1.00 | 0.00 | 0.35 | 1.60 |

Analyses are ordered according to increasing Se content.

4.4.2. Pyrargyrite, Ag$_{3}$SbS$_{3}$

Pyrargyrite crystals up to 5 mm in size and massive grain aggregates several cm in size, occurring (less abundantly than miargyrite) in milky quartz gangue associated with miargyrite and freibergite of ore (iii) or in cavities of the kutnohorite–quartz gangue of red ore (ii), associated with other Ag-Sb sulfides and pyrite. Only three samples of pyrargyrite were found in black ore (i) (Figure 2a). In polished sections pyrargyrite was found in nine samples (40 point analyses) as anhedral grains up to 30 μm. It often forms thin veinlets as much as 200 μm in length and 20 μm in width. It occurs as a filling of thin fissures in miargyrite in a close vicinity of Au-rich silver. It also occurs in drop-shaped inclusions of galena in pyrite of red ore (ii) where it replaces galena (Figure 14a). The chemical composition...
of pyrargyrite and the corresponding chemical formulae are given in Table 13. In comparison to miargyrite and stephanite (Figure 13b), the determined range of Se$_{S-1}$ substitution in pyrargyrite is limited, maximum is 0.13 apfu (1.82 wt.% in one analysis, but in all others does not exceed 0.70 wt.%). The found As contents in pyrargyrite (solid solution with proustite) are very low (up to 0.02 apfu, i.e., 0.21 wt.%), similar to As contents in all primary sulfosalts of the hypogene mineralization in Kutná Hora.

![Figure 14](image)

Figure 14. (a) An inclusion in pyrite (Py) of red ore (ii): stephanite (Ste), which is a prevailing mineral in the inclusion replaces pyrargyrite (Prg). Remnants of original galena (white spots) which was later replaced by pyrargyrite are visible at the bottom part of the grain. (b) Euhedral crystal in pyrite (Py) of red ore (ii) formed by two Ag-rich mineral phases: naumannite (Nau) is replaced by stephanite (Ste). Both back-scattered electron (BSE) images.

Table 13. EPMA data for pyrargyrite.

| Analyses | wt.% | apfu Σ7 Atoms |
|----------|------|---------------|
| 2329     | 59.10 0.00 0.00 22.77 0.00 0.00 17.51 99.38 2.99 0.00 0.00 1.02 0.00 0.00 0.00 0.00 0.00 2.98 |
| 2471     | 59.38 0.07 0.08 22.95 0.00 0.00 18.13 100.60 3.02 0.00 0.00 1.03 0.02 0.04 2.87 |
| 2528     | 60.14 0.12 0.00 22.18 0.00 0.11 17.90 100.66 3.00 0.00 0.01 0.98 0.00 0.01 3.00 |
| 2528     | 61.11 0.00 0.00 21.94 0.00 0.15 17.63 100.83 3.02 0.00 0.00 0.96 0.00 0.01 2.93 |
| 2622     | 59.22 0.06 0.10 22.67 0.21 0.64 16.70 99.60 3.02 0.00 0.00 1.03 0.02 0.04 2.87 |
| 2729     | 61.69 0.00 0.00 21.74 0.00 0.69 17.53 101.65 3.06 0.00 0.00 0.96 0.00 0.05 2.93 |

Analyses are ordered according to increasing Se content.

4.4.3. Pyrostilpnite, Ag$_5$SbS$_3$

Orange to bright red leaflets and coatings of pyrostilpnite on fractures of quartz gangue were described by Vepřek [53]. Later, Mrázek and Zeman [17] found orange-red elongated transparent crystals up to 4 mm in length with intensive lustre in cavities of quartz gangue from the Vein I and Vein A (ore (iii)), determined by X-ray diffraction.

In backscatter electron images, pyrostilpnite was not distinguished from its isochronous dimorph, pyrargyrite. However, orange crystals of pyrostilpnite under veinlets of pyrargyrite were observed in optical microscope.

4.4.4. Stephanite, Ag$_5$SbS$_4$

Stephanite occurs in red ore (ii) from the Vein B as rare anhedral grains up to 20 μm in size in fractures of miargyrite or as inclusions in miargyrite (Figure 2e), accompanied by exsolutions of pyrargyrite, itself being replaced by ancanthite. It belongs to later minerals in the studied association.
It also occurs among drop-shaped inclusions in pyrite of red ore (ii), often rich in selenium (as much as 9.8 wt.% of Se) (Figure 14a, b and Figure 20b) or veinlets in miargyrite of red ore (ii) (Figure 24a).

The chemical composition of stephanite and the corresponding chemical formulae are given in Table 14. One grain of stephanite is characteristic of a very high Se content of as much as 1.11 apfu (9.84 wt.%, not included in Table 14 due to a lower total). Thus, stephanite—together with miargyrite—is especially of selenium-containing members of this group [57]. Determined contents of Se in the range 0.22–0.44 apfu are lower than for minerals of polybasite group in the literature [56]; low contents of copper are characteristic especially of selenium-containing members of this group [57].

Table 14. EPMA data for stephanite.

| Analyses wt.%  | Ag   | Cd   | Sb   | As   | Se   | Total | S | Ag | Cd | Sb | As | Se | S |
|----------------|------|------|------|------|------|-------|---|----|----|----|----|----|---|
| 2343           | 68.62| 0.15 | 16.64| 0.13 | 0.00 | 16.03 | 101.57 | 4.98 | 0.01 | 1.07 | 0.01 | 0.00 | 3.91 |
| 2524           | 67.43| 0.22 | 14.31| 0.00 | 0.00 | 15.66 | 97.63  | 5.06 | 0.02 | 0.95 | 0.00 | 0.00 | 3.95 |
| 2525           | 67.76| 0.13 | 15.00| 0.02 | 0.00 | 16.18 | 99.10  | 4.99 | 0.01 | 0.98 | 0.00 | 0.00 | 4.01 |
| 2755           | 68.74| 0.00 | 14.07| 0.00 | 0.00 | 15.64 | 98.45  | 5.13 | 0.00 | 0.93 | 0.00 | 0.00 | 3.92 |
| 2732           | 69.39| 0.00 | 13.88| 0.00 | 1.18 | 15.37 | 99.81  | 5.13 | 0.00 | 0.91 | 0.00 | 0.12 | 3.82 |
| 2747           | 66.97| 0.00 | 14.43| 0.03 | 1.70 | 14.31 | 97.44  | 5.14 | 0.00 | 0.98 | 0.00 | 0.18 | 3.69 |

Analyses are ordered according to increasing Se content.

4.4.5. Polybasite, [Ag₆Cu₃S₆] [(Ag,Cu)₉(Sb,As)₂S₇]

Polybasite was found in four grains of two samples (8 point analyses) as very rare euhedral table-like crystals 40 µm in length and 10 µm in width, cutting across galena inclusions in pyrite of red ore (ii) (Figure 15a, b). Polybasite is in a close contact with Se-rich acanthite and both minerals replace galena. Associated minerals forming inclusions in pyrite but not in a direct contact with polybasite include argyrodite, pyrargyrite, aguilarite, clausthalite and naumannite.

Figure 15. (a) Euhedral tabular crystal of polybasite (Plb) associated with Se-rich acanthite (Aca). Both minerals replace galena (Gn). (b) Euhedral tabular crystal of polybasite (Plb) growing across galena, which occurs as anhedral inclusions up to several tens of µm in pyrite (Py) of red ore (ii). Both back-scattered electron (BSE) images.

Polybasite differs in minor but essential Cu content from chemically similar stephanite and also by a different (Ag + Cu)/(Sb + As) ratio. Copper contents of only 0.22–0.44 apfu are lower than for minerals of polybasite group in the literature [56]; low contents of copper are characteristic especially of selenium-containing members of this group [57]. Determined contents of Se in the range 0.07–0.76 wt.%, not included in Table 14 due to a lower total. The selenium analogue of stephanite—the mineral selenostephanite—was described (9.84 wt.%, not included in Table 14 due to a lower total). Thus, stephanite—together with miargyrite—is especially the mineral with the highest determined range of the SeS⁻₁ substitution among Ag-Sb-S mineral phases (Figure 13b). The selenium analogue of stephanite—the mineral selenostephanite—was described from two Russian deposits—Rudnaya Sopka, Chukotka [54] and Julietta, Magadan region [55]—and requires 17.3 or more wt.% of Se.

Both back-scattered electron (BSE) images.
0.07–0.76 apfu (Figure 13b) in samples from Padua mine are lower than the minimal limit (>1 Se apfu) for selenopolybasite [57]. The content of the pearceite component in studied sample is low and does not exceed 0.17 apfu As (0.55 wt.%). The chemical analyses of polybasite and corresponding empirical formulae are given in Table 15.

4.5. Minerals of the Tetrahedrite Series

Freibergite, Ag₆[4Cu₄Fe₂]Sb₄S₁₃₋ₓ

Freibergite, together with miargyrite, is the most abundant silver mineral observed in the studied material (193 analyses). Freibergite occurs as crystals several mm in size in cavities of quartz–kutnohorite gangue (red ore (ii)) or in cavities of milky white quartz (ore (iii)) or grain aggregates several cm in size associated with miargyrite and pyrargyrite (ores (ii) and (iii)). In polished sections, it was frequently found also in black ore (i), and it forms anhedral grains up to 300 µm in size. The grains are often zonal, growth zones differ by silver content, negatively correlated with the copper content. Freibergite grows together intimately with diaphorite and freieslebenite, usually being replaced by miargyrite. An example of freibergite in black ore (i) is shown in Figure 2c; freibergite in red ore (ii) is shown in Figure 16a,b; and ore (iii) is shown in Figure 2f.

The status of Ag-rich members of tetrahedrite group (freibergite, argentotennantite) and especially their boundaries with tetrahedrite and tennantite, is still being investigated [44]. Some authors have proposed a minimum content for freibergite of 4 apfu Ag [44,58], and a condition of Ag > Cu for argentotennantite (about 5 apfu Ag) [59]. On the basis of the results of crystal structure studies [58,60] and analyses of natural samples [61,62], Ag preferentially occupies the triangular A position with total content 6 apfu, and according to the present rules of mineralogical nomenclature [31], the boundary would be 3 apfu Ag [62].

Two groups of compositions were identified. The majority of analyses (Table 16) represent typical freibergite with more than 4 apfu of Ag. Its chemical composition is fairly monotonous with regard to Fe/Zn and Sb/As ratios. Iron is always dominant, and As is not present, as is the case with all sulfosalts in hypogene mineralization in Kutná Hora. Zonality phenomena are visible in some grains quite profoundly, however, differing only moderately in terms of Ag/Cu ratio. Ag contents were determined from 3.99 apfu (23.33 wt.%) to 7.25 apfu (38.61 wt.%) in freibergite, indicating that the placement of Ag not only in the A position (up to 6 apfu), but also to a limited degree in the B position (up to 1.25 apfu) takes place. Freibergite with as much as 46.4 wt.% of Ag (8.93 apfu) was described from the Rejzské písmo Lode in the Kutná Hora ore district [18]. This phase corresponds to the newly approved mineral rozhdestvenskayaite [63]. Ag and Cu contents show an excellent negative correlation (Figure 17a), which is in agreement with published results (e.g., [35,64,65]). In the case of freibergite below 6 apfu Ag, the rest of the A position is filled with copper. The B position, in addition to Ag contents (up to 0.40 apfu), is occupied by dominant Cu. In the C position, Fe (1.09–2.02 apfu) prevails over Zn (0.03–0.98 apfu), which is typical of freibergite (Figure 17b). Determined Ag/Cu ratios show no apparent correlation with Fe/Zn ratios. In the X position, the dominant Sb is in a part of analyses accompanied by negligible As, not exceeding 0.09 apfu (0.36 wt.%).

The second group of analyses corresponds to members at the boundary between freibergite and Ag-rich tetrahedrite. This member is very rare and was found only in one sample of black ore (i) as anhedral grains associated with galena, freieslebenite, diaphorite, owyheeite and Ag-excess fizelyite. Ag content varies from 17.41 to 18.48 wt.%, corresponding to 2.93 to 3.15 apfu Ag, which is appreciably less than a typical common member of the tetrahedrite series, which is freibergite on all lodes of the Kutná Hora ore district. The chemistry is similar to freibergite in the respect that iron prevails over zinc, no arsenic substitutes for antimony (Table 17), and the substitution of Se for S is non-existent, although surrounding minerals contain as much as 1.1 wt.% of Se.
Table 15. EPMA data for polybasite.

| Analyses | wt.% | apfu Σ29 Atoms |
|----------|------|----------------|
|          | Ag   | Cu  | Pb | Fe | Cd | Sb | As | Se | S  | Total  | Ag | Cu | Pb | Fe | Cd | Sb | As | Se | S  |
| 2589     | 71.20 | 0.61 | 0.51 | 0.30 | 0.13 | 10.72 | 0.04 | 0.95 | 14.97 | 99.43 | 15.36 | 0.22 | 0.06 | 0.13 | 0.03 | 2.05 | 0.01 | 0.28 | 10.87 |
| 2587     | 71.45 | 0.69 | 0.74 | 0.54 | 0.17 | 11.85 | 0.03 | 1.01 | 15.96 | 102.43 | 14.82 | 0.24 | 0.08 | 0.22 | 0.03 | 2.18 | 0.01 | 0.29 | 11.14 |
| 2595     | 70.62 | 1.11 | 0.08 | 0.72 | 0.14 | 9.67 | 0.55 | 2.61 | 14.81 | 100.31 | 14.97 | 0.40 | 0.01 | 0.30 | 0.03 | 1.82 | 0.17 | 0.76 | 10.56 |

Analyses are ordered according to increasing Se content.

Table 16. EPMA data for freibergite.

| Analyses | wt.% | apfu Σ29 atoms |
|----------|------|----------------|
|          | Ag   | Cu  | Fe | Zn | Sb | As | Se | S  | Total  | Ag | Cu | Fe | Zn | Sb | As | Se | S  | Ag/A | Cu/B |
| 2419     | 23.33 | 20.84 | 4.72 | 1.64 | 26.83 | 0.01 | 0.00 | 22.34 | 99.71 | 3.99 | 6.05 | 0.46 | 4.07 | 0.00 | 0.00 | 12.85 | 3.99 | 4.04 |
| 2547     | 26.62 | 18.16 | 5.07 | 1.64 | 26.72 | 0.03 | 0.13 | 22.68 | 101.04 | 4.54 | 5.25 | 1.67 | 4.03 | 0.01 | 0.03 | 13.00 | 4.54 | 3.79 |
| 2548     | 27.49 | 17.76 | 5.15 | 1.90 | 26.65 | 0.08 | 0.12 | 22.50 | 101.66 | 4.68 | 5.13 | 1.69 | 4.02 | 0.02 | 0.03 | 12.88 | 4.68 | 3.81 |
| 2549     | 27.83 | 17.54 | 4.95 | 1.72 | 26.74 | 0.00 | 0.13 | 22.42 | 101.32 | 4.76 | 5.10 | 1.64 | 4.06 | 0.01 | 0.03 | 12.91 | 4.76 | 3.86 |
| 2246     | 28.78 | 16.57 | 5.30 | 0.97 | 26.48 | 0.00 | 0.00 | 21.46 | 99.56 | 5.07 | 4.96 | 1.80 | 4.14 | 0.00 | 0.00 | 12.73 | 5.07 | 4.03 |
| 812      | 29.59 | 14.64 | 5.27 | 1.00 | 26.38 | 0.15 | 0.00 | 21.58 | 98.61 | 5.27 | 4.43 | 1.81 | 4.16 | 0.04 | 0.00 | 12.93 | 5.27 | 3.70 |
| 63       | 31.22 | 15.18 | 3.41 | 3.16 | 25.69 | 0.19 | 0.00 | 21.09 | 99.94 | 5.56 | 4.59 | 1.17 | 4.05 | 0.05 | 0.00 | 12.63 | 5.56 | 4.15 |
| 811      | 32.11 | 13.60 | 4.97 | 1.12 | 26.29 | 0.11 | 0.00 | 21.45 | 99.66 | 5.73 | 4.12 | 1.72 | 4.16 | 0.03 | 0.00 | 12.88 | 5.73 | 3.86 |
| 67       | 33.24 | 14.09 | 3.48 | 2.95 | 25.61 | 0.22 | 0.00 | 21.06 | 100.65 | 5.92 | 4.26 | 1.20 | 4.04 | 0.06 | 0.00 | 12.62 | 5.92 | 4.18 |
| 1461     | 33.55 | 13.78 | 5.01 | 1.07 | 25.99 | 0.11 | 0.00 | 20.91 | 100.01 | 6.02 | 4.19 | 1.74 | 4.07 | 0.03 | 0.00 | 12.62 | 6.00 | 4.19 |
| 42       | 33.87 | 13.64 | 3.56 | 2.63 | 25.63 | 0.21 | 0.00 | 20.52 | 100.06 | 6.12 | 4.19 | 1.24 | 4.11 | 0.05 | 0.00 | 12.48 | 6.00 | 4.19 |
| 36       | 34.60 | 13.45 | 3.75 | 2.30 | 25.69 | 0.23 | 0.00 | 20.65 | 100.67 | 6.22 | 4.11 | 1.30 | 4.09 | 0.06 | 0.00 | 12.50 | 6.00 | 4.11 |
| 2142     | 34.80 | 13.03 | 5.58 | 0.11 | 26.15 | 0.00 | 0.00 | 20.44 | 100.11 | 6.31 | 4.01 | 1.95 | 4.20 | 0.00 | 0.00 | 12.47 | 6.00 | 4.01 |
| 2140     | 36.99 | 12.32 | 5.40 | 0.09 | 24.60 | 0.00 | 0.00 | 19.67 | 99.07 | 6.85 | 3.87 | 1.93 | 4.03 | 0.00 | 0.00 | 12.25 | 6.00 | 3.87 |
| 1120     | 38.61 | 11.96 | 4.32 | 1.15 | 21.94 | 0.10 | 0.00 | 19.51 | 97.57 | 7.25 | 3.61 | 1.57 | 3.65 | 0.03 | 0.01 | 12.32 | 6.00 | 3.81 |

Ag/A–apfu of silver in triangular coordination; Cu/B–apfu f Cu$^{2+}$ in tetrahedral coordination; Analyses are ordered according to increasing Ag content.
Figure 16. (a) Fractured mass of porous sphalerite (dark grey) contains fissures filled by veinlets of freibergite (medium grey) with exsolutions of Se-rich miargyrite (15 wt.% of Se, light grey) and members of galena-clausthalite solid solution (white) from Gal70–Claus30 (15 wt.% of Se) to Claus78–Gal22 (20 wt.% of Se). (b) Freibergite (Frg) in quartz of red ore (ii) containing inclusions of clausthalite (Clh, 21.5% of Se) or members of galena-clausthalite solid solution (Gn, 14.2% of Se) and argyrodite (Agd, 9.8% of Se). Both back-scattered electron (BSE) images.

Figure 17. (a) Graph of Ag vs. Cu (apfu) for freibergite; (b) graph of Fe vs. Zn (apfu) for freibergite.

Table 17. EPMA data for Ag-rich tetrahedrite/freibergite.

| Analyses | Ag wt.% | Cu wt.% | Fe wt.% | Zn wt.% | Sb wt.% | S wt.% | Total | Ag apfu | Cu apfu | Fe apfu | Zn apfu | Sb apfu | S apfu | Ag/A ratio | Cu/B ratio |
|----------|---------|---------|---------|---------|---------|--------|-------|--------|---------|---------|---------|---------|---------|------------|------------|
| 2047     | 17.41   | 24.78   | 5.44    | 1.05    | 27.43   | 98.68  | 2.93  | 7.09   | 1.77    | 0.29    | 4.10    | 12.80   | 2.93    | 4.02       |            |
| 2045     | 17.84   | 24.41   | 5.50    | 1.08    | 27.64   | 99.12  | 3.00  | 6.97   | 1.78    | 0.30    | 4.12    | 12.81   | 3.00    | 3.97       |            |
| 2046     | 18.48   | 23.81   | 5.35    | 1.08    | 27.40   | 98.36  | 3.15  | 6.89   | 1.76    | 0.30    | 4.13    | 12.74   | 3.15    | 4.03       |            |

Ag/A—apfu of silver in triangular coordination; Cu/B—apfu of Cu$^{2+}$ in tetrahedral coordination; Analyses are ordered according to increasing Ag content.

A very interesting thing in the chemistry of freibergite and tetrahedrite is the fact that selenium does not enter the structure of freibergite, even if the grains of freibergite occur in a Se-rich environment, which was documented both in black ore (i) and red ore (ii). While all other associated sulfosalts take in selenium more or less eagerly, freibergite remains Se-free.
4.6. Ag-S, Ag-Se-S and Ag-Se Phases

4.6.1. Acanthite, Ag$_2$S

Acanthite occurs as anhedral grains, fillings of other silver minerals, or veinlets 50 µm wide and several hundred µm long, associated with pyrargyrite, allargentum and native silver (Figure 18a) in quartz–kutnohorite gangue of red ore (ii), where it originated from former argentite. It belongs to the latest minerals in the association. This acanthite shows no selenium content. The second mode of occurrence of acanthite is drop-like inclusions of up to 30 µm in pyrite of red ore (ii), which are characteristic of increased Se content with a continual transition to aguilarite and naumannite (Figure 18b–d). Occasionally, inhomogeneous grains with oscillating Se content occur. Grains of acanthite richest in selenium (with composition close to aguilarite) are usually under 10 x 10 µm. In the third mode of occurrence inclusions of galena in pyrite are partially replaced by acanthite, which has a significant selenium content. It is fairly frequent in red ore (ii), associated (but not in direct contact) with naumannite, clausthalite, argyrodite and aguilarite.

![Figure 18](image_url)

**Figure 18.** (a) Mass and veinlets of allargentum (Ala) and Sb-rich silver (Slv*); veinlets thicken up to form grains of pure Sb-free silver (Slv). Pyragyrite (Prg) forms euhedral masses and acanthite (Aca) forms veinlets and fillings around allargentum. Residues of original galena (Gn) are visible at the right side of the grain, the mineral is replaced by acanthite. (b) aguilarite (Agu, 18 wt.% of Se) replacing galena (Gn) in one of plentiful galena inclusions in pyrite of red ore (ii). Some of the inclusions are fully replaced by Se-rich acanthite (Aca*, 4 wt.% of Se), which forms a nearly continuous solid solution from acanthite with no Se (Aca) through Se-rich acanthite to aguilarite and naumannite. (c) diversity of inclusions in pyrite of red ore (ii); the larger inclusion shows the replacement of galena (white) by acanthite (dark grey). The smaller inclusion below is argyrodite. (d) large inclusion of Se-rich acanthite (Aca), inclusion of galena (Gn) and an inclusion of an unnamed Ag-Cu-S phase (Acs) in pyrite (Py) of red ore (ii).
Chemical composition of acanthite and corresponding chemical formulae are given in Table 18. Increased selenium contents are characteristic of the studied acanthite. In most cases, these are up to 0.13 apfu, some very small grains have as much as 0.30 apfu (8.83 wt.%) (Figure 19). With regard to the small size of grains, measured minor contents of Cu, Pb, Fe, Zn and Sb in some analytical points are probably influenced by surrounding phases.

### Table 18. EPMA data for acanthite.

| Analyses | Ag  | Cu  | Pb  | Fe  | Cd  | Se  | S   | Cl  | Total | Ag  | Cu  | Pb  | Fe  | Cd  | Se  | S   | Cl  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| 2814     | 86.85 | 0.13 | 0.00 | 0.00 | 0.00 | 12.16 | 0.00 | 99.39 | 2.03 | 0.01 | 0.00 | 0.00 | 0.00 | 0.96 | 0.00 | 0.00 |
| 2647     | 87.50 | 0.00 | 0.05 | 0.42 | 0.17 | 1.03 | 11.77 | 0.00 | 100.93 | 2.03 | 0.00 | 0.02 | 0.00 | 0.03 | 0.92 | 0.00 | 0.00 |
| 2646     | 85.66 | 0.00 | 0.09 | 0.47 | 0.22 | 1.21 | 11.06 | 0.00 | 98.71 | 2.04 | 0.00 | 0.02 | 0.00 | 0.04 | 0.89 | 0.00 | 0.00 |
| 2719     | 84.15 | 0.00 | 0.10 | 1.03 | 0.04 | 1.42 | 11.28 | 0.56 | 98.70 | 1.97 | 0.00 | 0.05 | 0.00 | 0.05 | 0.89 | 0.04 | 0.00 |
| 2623     | 83.18 | 0.00 | 0.18 | 0.03 | 0.16 | 3.64 | 12.36 | 0.00 | 99.82 | 1.91 | 0.00 | 0.00 | 0.00 | 0.11 | 0.96 | 0.00 | 0.00 |
| 2579     | 83.95 | 0.00 | 0.00 | 1.62 | 0.23 | 4.01 | 12.45 | 0.00 | 102.31 | 1.87 | 0.00 | 0.07 | 0.00 | 0.12 | 0.93 | 0.00 | 0.00 |
| 2596     | 84.13 | 0.05 | 0.05 | 0.06 | 0.18 | 3.98 | 11.65 | 0.00 | 100.67 | 1.94 | 0.00 | 0.03 | 0.00 | 0.13 | 0.90 | 0.00 | 0.00 |
| 2594     | 85.15 | 0.00 | 0.00 | 0.50 | 0.17 | 4.29 | 11.55 | 0.00 | 101.68 | 1.95 | 0.00 | 0.02 | 0.00 | 0.13 | 0.89 | 0.00 | 0.00 |
| 2601     | 79.66 | 0.33 | 0.77 | 0.05 | 0.06 | 3.83 | 8.29 | 0.00 | 98.27 | 1.97 | 0.01 | 0.01 | 0.00 | 0.30 | 0.69 | 0.00 | 0.00 |

Increased Fe and Pb contents are caused by surrounding galena or pyrite. Analyses are ordered according to increasing Se content.

![Graph Se vs. S (at.%) for acanthite, aguilarite and naumannite.](image)

**Figure 19.** Graph Se vs. S (at.%) for acanthite, aguilarite and naumannite.

4.6.2. Aguilarite, Ag₄SeS

Aguilarite was confirmed in one sample as a small anhedral grain 6 × 4 μm in a galena inclusion (25 μm across) in pyrite of red ore (ii) (Figure 18b); aguilarite replaces galena. The galena inclusion was surrounded by (but not in direct contact with) smaller inclusions—or semi-euhedral grains—of acanthite with variable selenium content (from zero to 4 wt.%). Plentiful inclusions in pyrite of this sample are formed—apart from predominant galena and occasional acanthite—by argyrodite, freibergite, (Ge,Se)-rich acanthite, clausthalite, naumannite, polybasite, pyrargyrite and unnamed Ag-Cu-S phases.
The chemical composition of aguilarite exhibits contents of Se in the range of 1.22–1.28 \( \text{apfu} \) (Table 19); with regard to the small size of grains, the measured minor contents of Pb and Fe are likely to be caused by surrounding phases. Aguilarite was defined by Bindi and Pingitore [66] as a member of the monoclinic solid solution acanthite–aguilarite with Se\( > \)S (more than 16.67 at.% Se), and at the same time, with Se contents below ca. 1.4 \( \text{apfu} \) (23.33 at.%), which represents a boundary for an orthorhombic S-rich naumannite (Figure 19).

### Table 19. EPMA data for aguilarite.

| Analyses | Ag   | Pb   | Fe   | Cd   | Se   | S   | Total | Ag | Pb | Fe | Cd | Se | S   |
|----------|------|------|------|------|------|-----|-------|----|----|----|----|----|-----|
| 2577     | 74.02| 1.64 | 1.84 | 0.20 | 17.59| 4.65| 99.94 | 0.04| 0.18| 0.01| 1.22| 0.79|
| 2578     | 75.50| 0.16 | 1.77 | 0.19 | 18.16| 3.62| 99.41 | 0.00| 0.18| 0.01| 1.28| 0.63|

Elevated levels of Pb and Fe are caused by surrounding galena or pyrite.

The nomenclature of mineral phases along the Ag\(_2\)S–Ag\(_2\)Se join was published by Bindi and Pingitore [66]. They suggest that two distinct solid solution series could exist: monoclinic “acanthite-type” series including aguilarite in the range Ag\(_2\)S–Ag\(_2\)S\(_{0.4}\)Se\(_{0.6}\), and an orthorhombic “naumannite-type” series between Ag\(_2\)S\(_{0.3}\)Se\(_{0.7}\)–Ag\(_2\)Se. The status of members with Se contents in the range 0.60–0.70 (or 1.2–1.4 for 6 \( \text{apfu} \) of aguilarite), which correspond to two-phase (monoclinic and orthorhombic) field as was described by Pingitore et al. [67] or Pal’yanova et al. [68] is still under debate. According to Kullerud et al. [69], there are two possible explanations—presence of metastable cubic high-temperature phase or mixtures of two submicroscopic phases formed during cooling of homogenous cubic phase below 80 °C. Natural minerals with compositions related to this two-phase field have also been reported [68,69].

The described aguilarite in Table 19 shows Se contents within the above-mentioned range, i.e., between 1.22 and 1.28 \( \text{apfu} \), corresponding to 0.61 and 0.64 \( \text{apfu} \), if calculated to 3 \( \text{apfu} \). However, it is impossible to decide whether a metastable phase or a mixture of two submicroscopic phases is present.

#### 4.6.3. Naumannite, Ag\(_2\)Se

Naumannite was found in four grains of three samples (9 point analyses). The mode of occurrence is very similar to aguilarite, i.e., in drop-like inclusions in massive pyrite of red ore (ii).

In the first sample, an inclusion of Se-rich miargyrite (8.7 wt.% of Se) 100 \( \mu \)m across in pyrite contains an euhedral grain of naumannite 30 \( \mu \)m across and a semi-euhedral grain of clausthalite. Clausthalite and naumannite are not in direct contact and both minerals replace Se-rich miargyrite (Figure 20a). The second grain occurs in a 20 \( \mu \)m inclusion in pyrite formed by clausthalite, Se-rich stephanite (9.8 wt.% of Se) and naumannite. Clausthalite appears to be the earliest mineral, replaced by both stephanite and naumannite. In the third sample, an inclusion in pyrite 30 \( \mu \)m across is formed by Se-rich stephanite (9.1 wt.% of Se), which is replaced by naumannite. The shape of the inclusion is not drop-like, but rather euhedral, following the crystal shape of stephanite (Figure 14b). The fourth sample occurs in a galena inclusion of 140 \( \mu \)m in pyrite. An anhedral grain of naumannite 6 \( \mu \)m across replaces galena at one of its edges.

Chemical composition of naumannite and corresponding chemical formulae are given in Table 20; the range of SSe\(_{-1}\) substitution in naumannite was determined to be 0.01–0.18 \( \text{apfu} \) (Figure 19). With regard to the small size of grains, minor measured contents of Pb and Fe in some analytical points are probably influenced by surrounding phases.
4.7.1. Argyrodite, Ag₈GeS₆

Argyrodite was found in nine grains of three samples (16 point analyses). It occurs as individual anhedral grains up to 40 μm among bubble-shaped inclusions in pyrite of red ore (ii) (Figure 18c). It was also found in sphalerite as a 12 μm grain bordering on freibergite in a galena inclusion of 45 μm (Figure 20b). Argyrodite and freibergite replace galena and are rimmed by pyrite. The replacement progresses from the clean-cut boundary with pyrite towards the centre of the galena inclusion, which is completely enclosed in sphalerite; in sphalerite associated with miargyrite and pyrite (Figure 12b); and as inclusions in freibergite with remnants of members of galena-clausthalite solid solution, which are replaced by freibergite (Figure 16b).

Chemical analyses of argyrodite are complicated due to the small size of the grains; the measured contents of Cu and Fe probably come from surrounding phases. Apart from major elements (Ag, Ge a S), significant contents of Se up to 0.69 apfu (4.93 wt.%) were found. The chemical composition and corresponding chemical formulae are given in Table 21. The discovery of germanium in the geochemistry of the Kutná Hora ore district shows another similarity with the Freiberg ore district, which is the type locality for argyrodite.

Table 20. EPMA data for naumannite.

| Analyses | wt.% | apfu Σ3 atoms |
|----------|------|---------------|
|          | Ag   | Pb  | Fe  | Cd  | Se  | S   | Total | Ag  | Pb  | Fe  | Cd  | Se  | S   | S | S |
| 2597     | 75.43 | 0.10 | 0.92 | 0.21 | 20.69 | 1.96 | 99.30 | 2.01 | 0.00 | 0.05 | 0.01 | 0.75 | 0.18 |
| 2696     | 74.20 | 0.00 | 1.06 | 0.17 | 23.94 | 0.31 | 99.66 | 2.02 | 0.00 | 0.06 | 0.00 | 0.89 | 0.03 |
| 2694     | 74.48 | 0.00 | 0.98 | 0.00 | 23.93 | 0.23 | 99.62 | 2.03 | 0.00 | 0.05 | 0.00 | 0.89 | 0.02 |
| 2698     | 74.10 | 0.00 | 0.66 | 0.05 | 23.74 | 0.20 | 98.76 | 2.04 | 0.00 | 0.04 | 0.00 | 0.89 | 0.02 |
| 2697     | 74.06 | 0.00 | 0.56 | 0.05 | 23.83 | 0.21 | 98.69 | 2.05 | 0.00 | 0.03 | 0.00 | 0.90 | 0.02 |
| 2696     | 74.06 | 0.00 | 0.56 | 0.05 | 23.83 | 0.21 | 98.69 | 2.05 | 0.00 | 0.03 | 0.00 | 0.90 | 0.02 |

4.7. Ag-Ge-S and Ag-Cu-S sulfides

4.7.1. Argyrodite, Ag₈GeS₆

Argyrodite was found in nine grains of three samples (16 point analyses). It occurs as individual anhedral grains up to 40 μm among bubble-shaped inclusions in pyrite of red ore (ii) (Figure 18c). It was also found in sphalerite as a 12 μm grain bordering on freibergite in a galena inclusion of 45 μm (Figure 20b). Argyrodite and freibergite replace galena and are rimmed by pyrite. The replacement progresses from the clean-cut boundary with pyrite towards the centre of the galena inclusion, which is completely enclosed in sphalerite; in sphalerite associated with miargyrite and pyrite (Figure 12b); and as inclusions in freibergite with remnants of members of galena-clausthalite solid solution, which are replaced by freibergite (Figure 16b).

Chemical analyses of argyrodite are complicated due to the small size of the grains; the measured contents of Cu and Fe probably come from surrounding phases. Apart from major elements (Ag, Ge a S), significant contents of Se up to 0.69 apfu (4.93 wt.%) were found. The chemical composition and corresponding chemical formulae are given in Table 21. The discovery of germanium in the geochemistry of the Kutná Hora ore district shows another similarity with the Freiberg ore district, which is the type locality for argyrodite.
Table 21. EPMA data for argyrodite.

| Analyses | Ag  | Cu  | Pb  | Fe  | Zn  | Ge  | Sb  | Se  | S   | Total | Ag  | Cu  | Pb  | Fe  | Zn  | Ge  | Sb  | Se  | S   |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 2614     | 78.19 | 0.00 | 0.11 | 1.84 | 0.00 | 5.66 | 0.13 | 0.10 | 17.72 | 103.84 | 7.80 | 0.01 | 0.01 | 0.35 | 0.00 | 0.838 | 0.01 | 0.01 | 5.94 |
| 2615     | 78.70 | 0.00 | 0.11 | 1.68 | 0.00 | 5.89 | 0.27 | 0.14 | 17.64 | 104.43 | 7.83 | 0.00 | 0.01 | 0.32 | 0.00 | 0.871 | 0.02 | 0.02 | 5.90 |
| 2616     | 73.91 | 0.00 | 1.11 | 1.40 | 0.00 | 6.95 | 0.60 | 0.70 | 17.05 | 101.81 | 7.57 | 0.00 | 0.06 | 0.28 | 0.00 | 1.06  | 0.05 | 0.10 | 5.87 |
| 2619     | 73.60 | 0.55 | 0.00 | 1.97 | 0.00 | 6.00 | 0.08 | 1.00 | 17.75 | 101.15 | 7.42 | 0.09 | 0.00 | 0.38 | 0.01 | 0.90  | 0.01 | 0.14 | 6.02 |
| 2707     | 72.59 | 0.54 | 0.25 | 2.31 | 0.00 | 5.53 | 0.00 | 1.03 | 18.04 | 100.63 | 7.31 | 0.09 | 0.01 | 0.45 | 0.01 | 0.83  | 0.00 | 0.14 | 6.12 |
| 2708     | 73.73 | 0.05 | 0.00 | 0.90 | 1.07 | 5.91 | 0.31 | 3.58 | 16.26 | 102.06 | 7.56 | 0.01 | 0.00 | 0.18 | 0.18 | 0.90  | 0.03 | 0.50 | 5.61 |

Elevated levels of Pb, Fe or Zn are caused by surrounding galena, pyrite or sphalerite. Analyses are ordered according to increasing Se content.
4.7.2. Ag-Cu-S Phases

Unnamed Ag-Cu-(S,Se) phases were found in five grains of three samples (23 point analyses) and occur in a very similar way to argyrodite as individual inclusions in pyrite, not in contact with any other mineral (Figures 18d and 21a). These phases were found as anhedral grains up to 50 × 30 μm among predominantly galena inclusions in pyrite in red ore (ii) (Figure 21b) and belong to the latest minerals. Similar to selenides and argyrodite, these grains are enclosed in pyrite growth zones with plentiful bubble-shaped inclusions.

![Figure 21](image-url)

**Figure 21.** (a) Oval inclusion of unnamed Ag-Cu-(S,Se) phase (Acs) in pyrite (Py) of red ore (ii). (b) bubble-shaped inclusions in pyrite of red ore (ii). Plentiful small inclusions in pyrite are formed—apart from predominant galena and occasional acanthite—by argyrodite, freibergite (Ge,Se)-rich acanthite, clausthalite, naumannite, polybasite, pyrargyrite and unnamed Ag-Cu-S phases. Both back-scattered electron (BSE) images.

A common feature of all analyses (Table 22) is that the metal/sulphur ratio is between 1.36 and 1.74, while all known Ag-Cu-S minerals have this ratio equal to 2. Higher contents of S + Se in the anionic part suggest a different structural arrangement than in known phases and/or a possible involvement of Cu²⁺ cation. The Ag and Cu contents with a clear negative correlation (Figure 22a) were observed. They differ from known phases in the Ag-Cu-S system with respect to: a) the Ag/Cu ratio, and b) higher contents of S + Se in the anionic part (Figure 22b); the contents of minor Se were determined to be between 2 and 5 at.%. With regard to the rarity of Ag-Cu-S phases and to the minimal size of grains which does not rule the influence of surrounding phases (especially contents of Fe and Zn), it cannot be decided whether the measured points belong to new mineral phases.

![Figure 22](image-url)

**Figure 22.** (a) Graph Ag vs. Cu (at.%) for Ag-Cu-S mineral phases; composition range for mckinstryite are given from [70]; (b) graph Cu/Ag vs. S + Se (at.%) for Ag-Cu-S mineral; composition range for mckinstryite are given from [70].
Table 2. EPMA data for unnamed Ag-Cu-S phases.

| Analyses | Ag  | Cu  | Pb  | Fe  | Cd  | Zn  | Se  | S   | Total | Ag  | Cu  | Pb  | Fe  | Cd  | Zn  | Se  | S   |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| 2653     | 78.57 | 3.64 | 0.00 | 0.67 | 0.09 | 0.00 | 2.17 | 13.85 | 98.99 | 57.88 | 4.55 | 0.01 | 0.95 | 0.06 | 0.00 | 2.18 | 34.33 |
| 2670     | 69.06 | 3.79 | 0.00 | 3.50 | 0.00 | 0.53 | 4.51 | 16.29 | 97.69 | 47.92 | 4.47 | 0.00 | 4.70 | 0.00 | 0.60 | 4.28 | 38.03 |
| 2664     | 75.73 | 4.91 | 0.19 | 0.88 | 0.17 | 0.20 | 4.76 | 12.72 | 99.57 | 55.82 | 6.14 | 0.07 | 1.26 | 0.12 | 0.25 | 4.80 | 31.53 |
| 2669     | 73.92 | 5.37 | 0.13 | 1.37 | 0.00 | 0.43 | 4.10 | 14.01 | 99.32 | 53.07 | 6.54 | 0.05 | 1.90 | 0.00 | 0.51 | 4.02 | 33.84 |
| 2668     | 74.92 | 5.41 | 0.11 | 1.46 | 0.05 | 0.41 | 4.39 | 14.14 | 100.88 | 53.03 | 6.50 | 0.04 | 2.00 | 0.03 | 0.48 | 4.24 | 33.66 |
| 2654     | 76.60 | 6.10 | 0.16 | 0.68 | 0.12 | 0.00 | 1.82 | 14.94 | 100.41 | 54.23 | 7.33 | 0.06 | 0.93 | 0.08 | 0.02 | 1.76 | 35.58 |
| 2649     | 72.54 | 7.46 | 0.19 | 0.84 | 0.15 | 0.00 | 2.60 | 15.09 | 98.86 | 51.23 | 8.94 | 0.07 | 1.14 | 0.10 | 0.04 | 2.51 | 35.85 |
| 2648     | 70.46 | 8.47 | 0.10 | 0.74 | 0.13 | 0.00 | 2.24 | 15.92 | 98.06 | 49.22 | 10.05 | 0.04 | 1.00 | 0.08 | 0.00 | 2.14 | 37.41 |
| 2650     | 68.35 | 8.89 | 0.19 | 1.07 | 0.08 | 0.00 | 3.51 | 15.18 | 97.26 | 48.25 | 10.65 | 0.07 | 1.46 | 0.05 | 0.00 | 3.38 | 36.04 |
| 2651     | 67.79 | 9.64 | 0.08 | 1.16 | 0.12 | 0.00 | 2.87 | 15.69 | 97.36 | 47.29 | 11.42 | 0.03 | 1.57 | 0.08 | 0.05 | 2.73 | 36.82 |
| 2734     | 60.24 | 15.60 | 0.22 | 1.45 | 0.10 | 0.00 | 2.21 | 18.11 | 97.92 | 39.15 | 17.21 | 0.07 | 1.82 | 0.06 | 0.00 | 1.96 | 39.59 |
| 2736     | 57.30 | 15.64 | 0.00 | 2.09 | 0.00 | 0.00 | 2.17 | 18.08 | 95.28 | 37.71 | 17.47 | 0.00 | 2.66 | 0.00 | 0.00 | 1.95 | 40.03 |

Elevated levels of Pb, Fe or Zn are caused by surrounding galena, pyrite or sphalerite. Analyses are ordered according to increasing Cu content.
4.8. Native Elements; Ag, Au Sulfides and Antimonides

4.8.1. Silver, Ag

Native silver occurs as yellow-white metallic aggregates several mm in size in cavities of the kutnohorite-quartz gangue of Vein B (red ore (ii)), associated with other silver minerals, namely with miargyrite, pyrargyrite and freibergite, and also in ore (iii) associated with pyragyrite, miargyrite and diaphorite. Silver occurs in two varieties, which differ with regard to Sb content: hypogene (primary) Sb-rich silver (Table 23) and later (mobilized) pure Sb-free native silver (Table 24). Polished sections of Sb-free silver were found as grains up to 50 µm in veinlets of Sb-rich silver several hundreds µm long, which form rims of masses of allargentum (Figure 18a). This pure native silver contains only traces of Hg, As, Fe and Cl. The more abundant Sb-rich silver is associated with pyrargyrite, acanthite, allargentum and Sb-free silver. Contents of Sb in the range 0.01–0.03 apfu (1.3–3.1 wt.%) are characteristic of this type of silver (Table 23, Figure 23).

Table 23. EPMA data for Sb-rich silver.

| Analyses | Ag  | Au  | Sb   | As  | Cl  | Total | Ag  | Au  | Sb  | As  | Cl  | Total |
|----------|-----|-----|------|-----|-----|-------|-----|-----|-----|-----|-----|-------|
| 2825     | 98.45 | 0.00 | 1.32  | 0.07 | 0.10 | 99.94  | 0.98 | 0.00 | 0.01 | 0.00 | 0.00 |
| 2827     | 98.49 | 0.00 | 1.89  | 0.00 | 0.11 | 100.49 | 0.98 | 0.00 | 0.02 | 0.00 | 0.00 |
| 2824     | 98.40 | 0.00 | 1.99  | 0.12 | 0.11 | 100.62 | 0.98 | 0.00 | 0.02 | 0.00 | 0.00 |
| 2813     | 98.16 | 0.00 | 2.10  | 0.11 | 0.11 | 100.48 | 0.97 | 0.00 | 0.02 | 0.00 | 0.00 |
| 2829     | 98.09 | 0.00 | 2.61  | 0.12 | 0.10 | 100.92 | 0.97 | 0.00 | 0.02 | 0.00 | 0.00 |
| 2844     | 97.16 | 0.00 | 2.73  | 0.05 | 0.10 | 100.49 | 0.97 | 0.00 | 0.02 | 0.00 | 0.00 |
| 2830     | 97.66 | 0.13 | 2.77  | 0.09 | 0.12 | 100.77 | 0.97 | 0.00 | 0.02 | 0.00 | 0.00 |
| 2838     | 97.17 | 0.09 | 2.92  | 0.09 | 0.13 | 100.40 | 0.97 | 0.00 | 0.03 | 0.00 | 0.00 |
| 2848     | 97.07 | 0.00 | 2.91  | 0.00 | 0.10 | 100.08 | 0.97 | 0.00 | 0.03 | 0.00 | 0.00 |
| 2833     | 97.53 | 0.00 | 2.99  | 0.15 | 0.12 | 100.79 | 0.97 | 0.00 | 0.03 | 0.00 | 0.00 |
| 2839     | 97.73 | 0.00 | 3.11  | 0.09 | 0.10 | 101.03 | 0.97 | 0.00 | 0.03 | 0.00 | 0.00 |

Analyses are ordered according to increasing Sb content.

Table 24. EPMA data for silver.

| Analyses | Ag   | Au   | Hg   | As   | Te   | Cl   | Total | Ag   | Au   | Hg   | As   | Te   | Cl   |
|----------|------|------|------|------|------|------|-------|------|------|------|------|------|------|
| 2865     | 101.59 | 0.00 | 0.10 | 0.16 | 0.11 | 0.13 | 102.09 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2866     | 101.61 | 0.06 | 0.00 | 0.07 | 0.12 | 0.11 | 101.97 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2867     | 101.62 | 0.00 | 0.00 | 0.09 | 0.12 | 0.11 | 101.94 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2868     | 101.53 | 0.00 | 0.20 | 0.10 | 0.10 | 0.13 | 102.06 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2828     | 100.47 | 0.08 | 0.00 | 0.11 | 0.00 | 0.10 | 100.76 | 0.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Interestingly, no native silver whatsoever occurs in plentiful bubble-like inclusions in pyrite—all are acanthite—with the exception of Au-rich silver (electrum).

4.8.2. Au-rich Silver (Ag,Au)

Au-rich silver (electrum) was found in 10 grains of four samples (23 point analyses) of red ore (ii), enclosed in miargyrite (8 grains up to 10 µm; Figure 24a) or sphalerite (2 grains up to 42 µm; Figure 24b). The phase richest in gold (and also the largest grain) was found as an anhedral grain of 42 x 25 µm enclosed in Fe-rich sphalerite; it contains 0.42–0.44 apfu Au (56–57 wt.%) (Figure 24b). Contents of Au were determined to be within the range 0.17–0.35 apfu (28–48 wt.%). Traces of Hg, Sb and Te (Table 25) were also identified; the minor contents of S determined are probably caused by surrounding phases.
Members of the Au-Ag solid solution (*electrum*) have been identified in the past from three lodes of Kutná Hora ore district on the basis of ore microscopy as allotriomorphic grains up 10 μm enclosed in freibergite, pyrargyrite or miagyrite. Only one occurrence was analysed chemically by emission spectral analysis [71].

### 4.8.3. Uyttenbogaardtite Ag₃AuS₂

Uyttenbogaardtite was found as one semi-euhedrall grain 9 × 6 μm in massive miagyrite of red ore (ii). The image in Figure 25a reveals that the grain contains minute inclusions of Au-rich silver (white spots, one larger one is visible at the left edge of the grain) with 51.0 wt.% of Au and 46.3 wt.% of Ag (corresponding to 35.7 at.% Au), which are probably responsible for the lower sulphur content in the measured points of uyttenbogaardtite. The top and right edge of the grain displays a hem resembling a reaction product. However, the hem is formed by uyttenbogaardtite with increased Sb content, a possible contamination from surrounding miagyrite.
This is the first occurrence of uytenboogaardtite in the Czech Republic. Recently, uytenboogaardtite was described from the selenium-rich Au-Ag epithermal deposit, Slovakia [72]. The chemistry of uytenboogaardtite from Kutná Hora (Table 26) shows a surplus of silver (3.16–3.33 at%) and a deficit of sulphur (1.66–1.87 at%) at all four analysed points. Two analyses show a surplus of gold (1.14 at%), and two show a deficit (0.77 and 0.87 at%). We assume that the lower sulphur contents compared to stoichiometry are caused by the fact that the grain is, in fact, a submicroscopic intergrowth of uytenboogaardtite with Au-rich silver, which is visible on the BSE photograph (Figure 25a).
4.8.4. Allargentum, Ag$_6$Sb

Allargentum (together with Sb-rich silver) is more abundant than native Sb-free silver in the hypogene mineralization. It is found as metallic white-yellow outgrowths, platelets or wire-like aggregates, usually up to several mm in size in the cavities of quartz–kutnohorite gangue of red ore (ii), associated with silver, pyrargyrite and miargyrite. In polished sections, it occurs as anhedral aggregates up to several hundred µm in size in miargyrite, associated with pyrargyrite and acanthite (Figure 18a).

The chemical composition of allargentum is relatively uniform and is close to the ideal formula (Table 27, Figure 23); only traces of Cl were identified. The empirical formula for studied allargentum samples on the basis of 7 apfu (mean of 10 analyses) can be expressed as Ag$_{5.95}$Sb$_{1.02}$Cl$_{0.02}$.

Table 27. EPMA data for allargentum.

| Analyses | Ag  | Au  | Sb  | As  | Cl  | Total | Ag  | Au  | Sb  | As  | Cl  |
|----------|-----|-----|-----|-----|-----|-------|-----|-----|-----|-----|-----|
| 2812     | 84.28 | 0.00 | 16.46 | 0.05 | 0.09 | 100.88 | 5.94 | 0.00 | 1.03 | 0.01 | 0.02 |
| 2832     | 84.75 | 0.00 | 16.29 | 0.00 | 0.09 | 101.13 | 5.96 | 0.00 | 1.01 | 0.00 | 0.02 |
| 2841     | 84.74 | 0.00 | 16.49 | 0.00 | 0.10 | 101.33 | 5.94 | 0.00 | 1.02 | 0.00 | 0.02 |
| 2842     | 84.21 | 0.00 | 16.42 | 0.00 | 0.10 | 100.73 | 5.94 | 0.00 | 1.03 | 0.00 | 0.02 |
| 2843     | 84.60 | 0.09 | 16.32 | 0.06 | 0.08 | 101.15 | 5.95 | 0.00 | 1.02 | 0.01 | 0.02 |
| 2846     | 84.29 | 0.00 | 16.30 | 0.00 | 0.10 | 100.69 | 5.95 | 0.00 | 1.02 | 0.00 | 0.02 |
| 2847     | 84.54 | 0.00 | 16.34 | 0.00 | 0.08 | 100.96 | 5.95 | 0.00 | 1.02 | 0.00 | 0.02 |

4.8.5. Au-rich Dyscrasite (Ag$_3$Au)$_3$Sb

Au-rich dyscrasite was found as one anhedral grain 60 x 30 µm in quartz, close to, but not in direct contact with, the massive miargyrite of red ore (ii) (Figure 25b).

The chemical analysis of dyscrasite (Table 28) revealed interesting contents of Au in the range 0.08–0.10 apfu (3.65–4.11 wt.%). A small deficit of Sb observed up to 0.08 apfu (Figure 23) corresponds to the ideal formula Ag$_{3+x}$Sb$_{1-x}$ proposed for dyscrasite by Scott [73] on the basis of crystal structure study.

Table 28. EPMA data for Au-rich dyscrasite.

| Analyses | Ag  | Au  | Sb  | Te  | S  | Total | Ag  | Au  | Sb  | Te  | S  |
|----------|-----|-----|-----|-----|----|-------|-----|-----|-----|-----|----|
| 2760     | 70.84 | 3.65 | 24.66 | 0.13 | 0.07 | 99.35 | 2.98 | 0.08 | 0.92 | 0.00 | 0.01 |
| 2761     | 69.83 | 3.92 | 26.50 | 0.06 | 0.05 | 100.35 | 2.92 | 0.09 | 0.98 | 0.00 | 0.01 |
| 2762     | 67.81 | 4.11 | 26.98 | 0.00 | 0.21 | 99.10 | 2.87 | 0.10 | 1.01 | 0.00 | 0.03 |
4.9. Galena–Clausthalite Solid Solution

4.9.1. Galena

Galena is a very frequent mineral in the Pb-rich black ore (i) from Vein B. It occurs as typical lead-grey cleavable grain aggregates several cm in size associated with other sulfides, occasionally as crystals in cavities. In polished sections, it was frequently found as the earliest mineral associated with boulangerite, freieslebenite, diaphorite, owyheeite, andorite group minerals, miargyrite and freibergite (Figure 2a–c,e, Figure 4, Figure 5c,d, Figure 8, Figure 10b, Figure 12a).

It is also frequently found in the red ore type (ii) as plentiful bubble-shaped inclusions in pyrite (Figure 21b), and also as idiomorphic grains; usually, it is the earliest mineral. Very frequently, it occurs as filling of bubble-shaped inclusions in the pyrite of red ore (ii) (Figure 15a,b, Figure 16b, Figure 18b,c,d, Figure 20a,b, Figure 21a,b). It also occurs in ore (iii) (Figure 2f). Increased Se contents (Table 29) were found only in small grains of galena (up to 20 µm across), associated with various Ag-Pb-Sb sulfosalts. Significantly increased Ag contents (up to 12.34 wt.%) were occasionally identified (34 points above 1 wt.% of Ag). These were found to be positively correlated with Sb contents (Figure 26a) and considerably higher than previously reported in the literature from this locality (0.10–0.21 wt.% [13,35]). Ag and Sb enter the structure of galena probably by the same mechanism as Ag and Bi in PbS_SS, i.e., galena - matildite solid solution [74,75]. The maximum values of Ag and Sb in the galena grains are 0.22 apfu and 0.23 apfu. Such a high degree of substitution was observed only in several grains and corresponds to the highest contents of PbS_SS ([74,76,77]. In most studied galena grains, the contents of Ag do not exceed 0.12 apfu; a similar range of Ag + (Bi,Sb) → 2Pb substations in PbS_SS are known from other occurrences around the world [23,74,75,77]. Measured contents of Se in galena (Table 29) are substantially higher than previously published data (0.14 wt.% Se [13]) and suggest an unlimited SeS−1 substitution in galena – clausthalite solid solution (Figure 26b); as mentioned before, higher Se contents were determined for smaller aggregates of galena, usually not exceeding 20 µm.

| Analyses | wt.% | apfu Σ2 atom |
|----------|------|--------------|
|          | Ag   | Cu | Pb   | Sb  | Se  | S   | Total | Ag | Cu | Pb | Sb  | Se  | S   |          |
| 2467     | 0.04 | 0.00 | 85.74 | 0.15 | 0.00 | 13.35 | 99.29 | 0.00 | 0.00 | 0.99 | 0.00 | 0.00 | 1.00 |
| 2013     | 0.09 | 0.05 | 85.80 | 0.13 | 0.19 | 13.49 | 99.75 | 0.00 | 0.00 | 0.98 | 0.00 | 0.01 | 1.00 |
| 857      | 0.00 | 0.00 | 85.81 | 0.19 | 0.44 | 13.59 | 100.04 | 0.00 | 0.00 | 0.98 | 0.00 | 0.01 | 1.00 |
| 2215     | 0.28 | 0.00 | 84.26 | 0.78 | 1.10 | 13.23 | 99.65 | 0.01 | 0.00 | 0.96 | 0.02 | 0.03 | 0.98 |
| 372      | 0.88 | 0.00 | 83.74 | 1.06 | 1.53 | 13.18 | 100.38 | 0.02 | 0.00 | 0.94 | 0.02 | 0.05 | 0.96 |
| 1264     | 0.21 | 0.00 | 83.85 | 0.28 | 2.57 | 12.38 | 99.29 | 0.00 | 0.00 | 0.97 | 0.01 | 0.08 | 0.93 |
| 2266     | 1.37 | 0.00 | 82.57 | 0.08 | 3.34 | 11.91 | 99.27 | 0.03 | 0.00 | 0.96 | 0.00 | 0.10 | 0.89 |
| 1494     | 0.08 | 0.00 | 84.30 | 0.16 | 3.64 | 11.92 | 100.11 | 0.00 | 0.00 | 0.98 | 0.00 | 0.11 | 0.90 |
| 23       | 0.13 | 0.31 | 84.51 | 0.09 | 3.83 | 12.03 | 100.90 | 0.00 | 0.01 | 0.97 | 0.00 | 0.12 | 0.89 |
| 2264     | 1.67 | 0.00 | 82.73 | 0.09 | 4.63 | 11.54 | 100.66 | 0.04 | 0.00 | 0.95 | 0.00 | 0.14 | 0.86 |
| 2315     | 1.29 | 0.00 | 82.87 | 0.07 | 5.10 | 10.84 | 100.17 | 0.03 | 0.00 | 0.98 | 0.00 | 0.16 | 0.82 |
| 22       | 0.20 | 0.31 | 83.63 | 0.08 | 5.38 | 11.12 | 100.72 | 0.00 | 0.01 | 0.97 | 0.00 | 0.16 | 0.84 |
| 2265     | 1.53 | 0.00 | 81.15 | 0.08 | 6.57 | 10.68 | 100.01 | 0.03 | 0.00 | 0.95 | 0.00 | 0.20 | 0.81 |
| 754      | 0.05 | 0.00 | 82.87 | 0.12 | 6.67 | 10.55 | 100.26 | 0.00 | 0.00 | 0.98 | 0.00 | 0.21 | 0.81 |
| 2314     | 1.01 | 0.00 | 82.32 | 0.06 | 6.82 | 9.98 | 100.19 | 0.02 | 0.00 | 0.98 | 0.00 | 0.21 | 0.77 |
| 1262     | 0.30 | 0.00 | 79.39 | 0.32 | 14.02 | 7.09 | 101.12 | 0.01 | 0.00 | 0.97 | 0.01 | 0.45 | 0.56 |

Analyses are ordered according to increasing Se content.
4.9.2. Clausthalite

Clausthalite is the most frequently occurring selenide mineral. It was found in both black ore (i) (Figure 27) (two samples, 10 point analyses) and, even more often, in red ore (ii) (four samples, 10 point analyses). The mineral was found as anhedral grains in fractures in freebergite filled in by miargyrite in red ore (ii) (Figure 16a). This miargyrite shows increased amounts of selenium and belongs to the latest minerals of the association. Other clausthalite grains are observed in bubble-shaped inclusions in pyrite of red ore (ii) (Figure 16b, Figure 20a) in association with Se-rich galena, accompanied by other minerals present in these inclusions (see aguilarite). Clausthalite was identified among compositions corresponding to the galena-clausthalite solid solution in black ore (i) as inclusions up to 50 μm in Se-free freieslebenite, which is replaced by clausthalite. Generally, members of the clausthalite-galena solid solution occurring in black ore (i) are accompanied by galena and Pb-Sb-(Ag) sulfosalts. Often a common trend is that smaller grains are Se-rich galena or clausthalite and larger grains of galena are generally Se-free.

Figure 26. (a) Graph Ag vs Sb (apfu) for members of galena – clausthalite solid solution. (b) graph Se vs S (apfu) for members of galena – clausthalite solid solution.

Figure 27. The general succession in Se-enriched black ore (i); clausthalite (Clh—16 wt.% of Se) and Se-rich galena (Gn, 2% Se) replaced by freieslebenite (Frs, 0.3% Se) and diaforite (Dia, 3.5% of Se). Back-scattered electron (BSE) image.
It has to be noted that no sulphur-free clausthalite was found in any of the measured samples. Sulphur contents in clausthalite (Table 30) range between 0.10–0.50 apfu (4.87–6.28 wt.%) (Figure 26b). An unlimited miscibility among clausthalite and galena was observed in experimental studies of phase relations in this system at temperatures above 300 °C [78–80]. The extrapolation of thermodynamic data for end members enables to envisage the existence of a complete solid solution PbSe–PbS up to temperatures of about 100 °C [79,80]. The existence of a complete isomorphous series PbS–PbSe in natural samples was described for the first time by Coleman [81], who studied samples from uranium–vanadium deposits in the area of Colorado Plateau, and later, it was confirmed by the research of samples from the deposits of Niederschlema–Alberoda [82], Moldava [83] and Potůčky [84] in Krušné hory Mountains or Běstvina in Železné hory Mountains [85]. Unlike coexisting galena, clausthalite contains very rarely increased contents of Ag (and Sb), not exceeding 0.11 apfu or 0.04 apfu, respectively (Figure 28). In Table 30, the contents of Ag and Sb are negligible.

| Analyses | wt.% | apfu Σ2 atom |  |
|----------|------|--------------|---|
|          | Ag   | Pb | Zn | Sb | Se | S | Total | Ag | Pb | Zn | Sb | Se | S |
| 303      | 0.19 | 77.35 | 0.50 | 0.09 | 16.35 | 6.36 | 100.83 | 0.00 | 0.94 | 0.02 | 0.00 | 0.52 | 0.50 |
| 239      | 0.05 | 78.52 | 0.41 | 0.06 | 16.32 | 5.90 | 101.26 | 0.00 | 0.97 | 0.02 | 0.00 | 0.53 | 0.47 |
| 1263     | 0.00 | 78.73 | 0.00 | 0.08 | 17.01 | 5.62 | 101.44 | 0.00 | 0.98 | 0.00 | 0.00 | 0.56 | 0.45 |
| 1255     | 0.05 | 78.43 | 0.00 | 0.10 | 17.60 | 5.66 | 101.83 | 0.00 | 0.98 | 0.00 | 0.00 | 0.58 | 0.43 |
| 1260     | 0.06 | 77.86 | 0.00 | 0.07 | 18.36 | 4.94 | 101.29 | 0.00 | 0.98 | 0.00 | 0.00 | 0.61 | 0.40 |
| 1261     | 0.00 | 76.47 | 0.00 | 0.08 | 18.74 | 4.87 | 100.16 | 0.00 | 0.97 | 0.00 | 0.00 | 0.62 | 0.40 |

Analyses are ordered according to increasing Se content.

![Figure 28](image-url) Graph Se/(Se + S) vs. (Ag + Sb)/(Ag + Sb + Pb) (apfu) for members of galena – clausthalite solid solution.

5. Discussion

5.1. Succession of Crystalization

The ore mineralization of the whole Kutná Hora ore district originated in several stages, separated by tectonic movements [26]. Each stage is subdivided into mineralization sequences, divided by weaker tectonic events or by distinct metasomatic processes. The similarity of the Kutná Hora [26] and
Freiberg [29] districts leads us to compare the nomenclature of the succession schemes in both districts (Table 31).

| Stage | Kutná Hora Sequence | Freiberg [29] Sequence |
|-------|----------------------|------------------------|
| I     | Ia. Fe-As            | Fe-As                  |
|       | Ib. Zn-Sn-Cu-Fe     | Zn-Sn-Cu               |
|       | lc. 1st carbonate    |                         |
| II    | IIa. Pb-Ag          | Pb-Ag                  |
|       | IIb. 2nd carbonate   |                         |
| III   | IIIa. Ag-Sb         | Ag-Sb                  |
|       | IIIb. Sb-Fe         |                         |
| IV    | quartz–pyrite–calcite|                         |

‘kb’—“kiesig-blendige Bleierzformation”; ‘eb’, ‘eq’—“edle Braunspatformation”; “edle Quarzformation”.

The veins of northern “pyrite-rich” lodes are characterized by the presence of the first two stages: Fe-As sequence (Ia); Zn-Sn-Cu-Fe sequence (Ib) and Pb-Ag sequence (IIa). Also present in northern lodes—though on smaller scale than in the south—is the later third stage: Ag-Sb sequence (IIIA) and Sb-Fe sequence (IIIB). On the contrary, the southern “silver-rich” lodes are characterized by a much smaller presence of the first two stages and a complete absence of Sn in Ib sequence and an almost exclusive representation of the stage III with frequent kutnohorite in gangue [8,86].

The Oselské pásma Lode, including the newly studied mineralization of Anthony of Padua mine (this paper) are a typical example of southern “silver-rich” lodes and the origin of this ore mineralization is bound to the youngest Ag–Sb sequence (IIIA). On the basis of published data as well as of new study (this paper), it was possible to single out several fundamental types (kinds) of ore: the Pb-rich black ore (i); the Ag-rich red ore (ii) in quartz–kutnohorite gangue; the Ag-rich ore (iii) in quartz gangue (see Section 4.1). Several hundred BSE images of seventy measured polished sections were examined and conclusions regarding associations and parageneses drawn. The succession of minerals in individual samples was determined where possible. Several trends, general features and repeated patterns were observed. The general succession follows the trend from Pb-rich phases to Pb-poorer (Ag-richer) phases. The earliest mineral in all three types of ore is galena.

(i) black ore—Pb-rich black ore in quartz with the general succession: galena – boulangerite (= jamesonite) – owyheeite – fizelyite – Ag-excess fizelyite – andorite IV – andorite VI – freieslebenite – diaporite – miargyrite – freibergite. This belongs to Ag-Sb sequence (IIIA), corresponding in the Freiberg succession scheme to Ag-Sb sequence of ‘eb’ ore type or the transitional ore type between ‘kb’ and ‘eb’, with an overprint of Se mineralization.

(ii) red ore—the Ag-rich red ore in kutnohorite + quartz. Three succession patterns are noticeable: one is galena – diaporite – freibergite – miargyrite – pyragyrite – stephanite – polybasite – acanthite; the second is galena – allargentum – pyragyrite – Sb-rich silver – silver (Sb-free) – acanthite; and the third is galena – freibergite – argyrodite – unnamed Ag-Cu-S phases (a reverse trend of argyrodite being replaced by freibergite was occasionally observed).

Concerning the position of gold alloys in the succession, the only observable examples are: Au-rich silver – uytenbogaardtite – miargyrite; sphalerite – Au-rich silver – freibergite; and Au-rich silver – miargyrite. This corresponds to Ag-Sb sequence IIIa, with overprints of Se, Ge and Au mineralizations, corresponding to ‘eb’ ore type, and the Ag-Sb sequence in Freiberg.

(iii) Ag-rich ore in milky quartz consists of crystals in cavities, bands and lenses of Ag minerals (mainly miargyrite), base sulfides are scarce. The usual succession is: galena – freieslebenite – diaporite – freibergite – miargyrite – pyragyrite/pyrostilpnite – stephanite – acanthite. It belongs to Ag-Sb
sequence III, with a weaker overprint of Se mineralization; corresponds to ‘eq’ ore type, Ag-Sb sequence in Freiberg.

The second, parallel succession scheme progresses from Se-free through Se-poor to Se-rich phases, such as: galena – members of galena - clausthalite solid solution – clausthalite; miargyrite – Se-rich miargyrite; acanthite – aguilarite – naumannite etc.

The mutual relationship between the three ores (i, ii and iii) is difficult to assess with regard to their occurrences in different veins. The authors of this article are of the opinion that the Pb-rich black ore (i) is the earliest of the three, followed by (ii) and (iii).

5.2. Discussion of the Formation Conditions

The Kutná Hora ore district is considered a typical example of postmagmatic sulfide base-metal mineralization of late Variscan age (Early Permian; [87]), analogous to the ‘kb + eb’ ore types (mineralizations) of Freiberg in Saxony, Germany [28,29]. Silver minerals (‘eb’, the Ag-Sb sequence in Freiberg) in the whole Kutná Hora ore district occur mostly on independent younger structures (Ag-Sb sequence IIIa) within the vein system; marked differences between the southern (dominant stage III (i.e.’eb’ and ‘eq’ ore type), weaker stage II (‘kb’) and northern lodes (dominant stage I and II (‘kb’), weaker stage III (‘eq’)) are primarily caused by a different geological (petrological, tectonic) structure of both parts [26]. Bernard and Žák [88] suggested that mineralization of Kutná Hora ore district generally originated at high temperatures (430 ± 80 °C + ‘kb’ stage); younger parts of the mineralization (‘eb/eq’ stage) were colder (<190 °C; [89]).

According to Seifert and Sandmann [29] an analogous Ag-Sb mineralization from the Freiberg district (‘eb’ ore type) originated at temperatures between 300–120 °C. They also mention possible mineralogical and geochemical similarities to epithermal-style Ag-Au mineralization [90,91]. The similarity of the studied Ag-Sb mineralization from southern “silver-rich” lodes of the Kutná Hora ore district with the ‘eb’ ore type of the Freiberg district is highlighted by the newly discovered germanium-bearing mineral argyrodite and by Au and Se presence in Kutná Hora correlating with the argyrodite occurrence and locally increased Au and Se contents in ‘eb’ ores of the Freiberg district [29].

The character of the discovered selenium mineralization (i.e., increased selenium contents in Ag- and Pb-Sb sulfosalts, the occurrence of minerals of galena – clausthalite solid solution, and Se-rich acanthite, aguilarite and naumannite) indicates the formation from hydrothermal fluids with \( f_{O_2} \) slightly above or close to hematite - magnetite buffer and the \( f_{Se_2/S_2} \) ratio close to unity. The presence of minerals of galena – clausthalite solid solution shows that the upper values of the \( f_{Se_2/S_2} \) ratio were more likely controlled by the galena – clausthalite buffer, which is still close to unity [92,93]. The occurrence of naumannite and acanthite which was deposited together with silver and Ag-sulfosalts requires conditions close to the native Ag-naumannite + acanthite invariant point [93,94]. Together with observed minerals of the galena – clausthalite solid solution it is possible to define a \( f_{Se_2} \) range of −23 to −26 and a \( f_{S_2} \) range of −21 to −22, respectively [93,94]. These values correspond very well with conditions published for selenide-bearing Au-Ag epithermal deposits by Simon et al. [93]. Although Kutná Hora ore district including Anthony of Padua mine is not a volcanic low-sulfidation epithermal deposit, the studied mineralization shows many similar features.

The source of selenium is probably in the bodies of (meta) ultrabasic rocks (serpentinites) frequently found by boreholes in southern “silver” lodes both south of town, as well as in its historic centre. The topomineral properties of these rocks may enable to pre-concentrate selenium which was released into hydrothermal fluids during tectonic events. The amphibolite from the quarry of Markovice, 10 km SE of Kutná Hora, known up to now only for the occurrence of zeolites, was recently found to contain selenides, tellurides and native tellurium [95,96]. The origin of selenides and tellurides from this locality is assumed to be related to (meta) ultrabasic rocks cutting through amphibolite rocks. A similar situation is also known from the northern part of the Kongsberg deposit, Norway [97].
6. Conclusions

(1) The previously unknown selenium mineralization (clausthalite, naumannite, aguilarite) and increased selenium contents in Ag- and Pb-Sb sulfosalts were determined in hydrothermal ore veins from Anthony of Padua mine near Poličany. These veins are part of the Oselské pásma Lode, one of the southern “silver-rich” lodes of the historic Kutná Hora ore district. The determined contents of Se in Ag- and Pb-Sb sulfosalts belong to the highest ever found worldwide.

(2) A suite of more than twenty silver minerals were determined in samples from Anthony of Padua mine: Ag-Pb-Sb sulfosalts (Ag-excess fizelyite, fizelyite, andorite IV, andorite VI, diaphorite, freieslebenite, owyheeite), Ag-Sb-(Cu)-sulfosalts (miargyrite, pyrargyrite, stephanite, polybasite, freibergite, Ag-rich tetrahedrite), Ag-sulfides and selenides (acanthite, aguilarite, naumannite, argyrodite), native elements, Ag, Au sulfides and antimonides (native silver and its Sb- or Au-rich variety, allargentum, Au-rich dyscrasite, uyttenbogaardtite) and unnamed Ag-poor Ag-Pb-Sb sulfosalts and Ag-Cu-S mineral phases. The Pb-Sb sulfosalts (boulangerite, sensemyite, jamesonite), and lead sulfide and selenide (members of galena – clausthalite solid solution) were also determined.

(3) Three kinds of ore were identified in studied samples: Pb-rich black ore (i), Ag-rich red ore (ii) in quartz–kutnohorite gangue, and Ag-rich ore (iii) in quartz gangue without sulfides. The general succession follows the trend from Pb-rich phases to Pb-poorer and Ag-richer phases. The earliest mineral is galena. The general successions scheme is for the Pb-rich black ore (i) as follows: galena – boulangerite (– jamesonite) – owyheeite – fizelyite – Ag-excess fizelyite – andorite IV – andorite VI – freieslebenite – diaphorite – freibergite. For the Ag-rich red ore (ii) and ore (iii), the most prominent pattern is galena – diaphorite – freibergite – miargyrite – pyrargyrite – stephanite – polybasite – acanthite. The parallel succession scheme progresses from Se-poor to Se-rich phases, for example, galena – members of galena - clausthalite solid solution – clausthalite; miargyrite – Se-rich miargyrite; acanthite – aguilarite – naumannite; etc.

(4) The observed Ag-rich mineral association provides an insight into the character of exploited ore on historic silver-rich lodes from the south of the Kutná Hora ore district, such as Oselské pásma Lode and Roveňské pásma Lode, which were the main silver deposits of Kutná Hora district in the 14th century. It is evident that silver minerals such as miargyrite and freibergite were the main sources of silver, and not the alleged low contents of Ag in base-metal sulfides (most frequently as inclusions of Ag minerals) like on northern lodes.

(5) The origin of economic silver mineralization of southern “silver-rich” lodes of the Kutná Hora district is bound primarily to the youngest Ag-Sb sequence IIIa, corresponding to the Ag-Sb sequence of the ‘eb/eq’ ore types in the Freiberg succession scheme. Earlier stages with base sulfide sequences, e.g., Zn-Sn-Cu-Fe sequence Ib and Pb-Ag sequence IIa, corresponding to the ‘kb’ ore type, which are abundantly present on lodes in the northern part of the Kutná Hora district, are much less developed (Pb-Ag sequence IIa) or missing (Zn-Sn-Cu-Fe sequence Ib). The described Ag-Sb mineralization of the Kutná Hora ore district is analogous to the Ag-Sb sequence of the younger ‘eb/eq’ ore type (mineralization) of the Freiberg district, Saxony, Germany, including a local minority presence of Ge, Au and Se minerals.

(6) The ore mineralization of the Kutná Hora ore district is a typical example of postmagmatic sulfide hydrothermal mineralization of late Variscan age. The Ag-rich mineralization of southern “silver-rich” lodes originated under temperatures significantly lower (< 190 °C) than the earlier mineralization of northern lodes (430 ± 80 °C); lower temperatures (300–120 °C) are stated in the literature for the origin of the analogous ‘eb’ mineralization (ore type) of the Freiberg district, Saxony, Germany.

(7) The association found between selenides and other Se-bearing mineral phases indicates hydrothermal fluids with fO2 slightly above or close to hematite-magnetite buffer and fSe2/F2 ratio close than unity: the ranges are -23 to -26 and -21 to -22 for fSe2 and fS2, respectively. These values correspond very well to conditions published for selenide-bearing Au-Ag epithermal deposits. The mineralogical and geochemical similarities of the entirety of the latest ‘eb’ ore type (mineralization) of the Freiberg ore district and the low-sulfidation epithermal-style Ag–Au mineralization have been published previously.
(8) The source of selenium in Kutná Hora is probably related to the bodies of (meta)ultrabasics (serpentinites) frequently found by boreholes in southern “silver” lodes both south of town and in its historic centre. The topomineral properties of these rocks may enable to pre-concentrate selenium which was released into hydrothermal fluids during tectonic events.

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