Original paper

An unusual Ni–Sb–Ag–Au association of ullmannite, allargentum, Au-rich silver and Au-bearing dyscrasite from Oselské pásmo “silver” Lode of Kutná Hora Pb–Zn–Ag ore district (Czech Republic)

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A rare and unusual Ni–Sb–Ag–Au association of ullmannite, NiSbS, associated with allargentum, Ag6Sb, Au-rich silver, Au9.7Ag85.0Sb2.9, and Au-bearing dyscrasite was found in medieval mine dump material of the Oselské pásmo “silver” lode of the historic Kutná Hora Pb–Zn–Ag ore district. Ullmannite is the first and only Ni sulphide found in the base-metal paragenesis of otherwise exclusively Ag–(Cu)–(Pb)–Sb sulphosalts. No other nickel mineral is known from this base-metal ore district. The mineral was identified in two polished sections of one sample as anhedral grains up to 50 µm across enclosed in allargentum. The average chemical composition of ullmannite Ni 26.76–27.17, Sb 57.80–59.17, S 15.14–15.28 wt. % corresponds to the empirical formula Ni0.98Sb1.01As0.01S1.00 on the basis of Ni + Sb + S = 3 apfu, i.e. it is close to the ideal formula with only trace contents of As. Au-rich silver with 15.52–16.34 wt. % of gold was found in association with freibergite and pyrargyrite as anhedral inclusions up to c. 5 µm across. The chemical composition corresponds to Au9.7Ag85.0Sb2.9 on the basis of 100 apfu. One more gold-containing phase was determined: Au-bearing dyscrasite with ~0.7 wt. % of Au. The sample also produced an example of Ag-rich “bonanza” with stephanite, acanthite, pyrargyrite and miargyrite. The likely source of nickel and gold were the serpentinized ultrabasic bodies, cut by the “silver” lodes in the South of the ore district. The serpentinites contain 2000 ppm of Ni and low but stable contents of Au. Penetration of hydrothermal fluids could have caused the mobilization of nickel and gold in serpentinites and in earlier ore mineralization (arsenopyrite). This process resulted in the breakdown of earlier silver minerals while allargentum, dyscrasite and stephanite crystallized. The discovery of Ni–Sb–Ag–Au association in Kutná Hora ore district sheds new light on the elemental variability of this hydrothermal vein-type deposit of Variscan age.

Keywords: ullmannite, allargentum, Au-rich silver, Au-bearing dyscrasite, chemistry, Kutná Hora ore district

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1. Introduction

Ullmannite is a nickel–antimony sulphide mineral with formula NiSbS. Considerable substitution occurs by cobalt and iron in the nickel site along with bismuth and arsenic in the antimony site. The mineral is usually associated with nickeline in the Ag–Co–Ni veins (Gowganda, Ontario, Canada; Williama, New South Wales, Australia) or in Ni–As veins at Lülling (Austria). It occurs in Pb–Zn veins of Harz, Germany (Bernard 1992). In the Czech Republic, crystals of ullmannite up to 1 cm were found in Pb–Zn quartz veins at Kůše near Stříbro, Western Bohemia (Bernard 1992). In the current work, we describe an interesting and unusual occurrence of this mineral phase in a Ni–Sb–Ag–Au association with allargentum, Au-rich silver and Au-bearing dyscrasite from the Kutná Hora mining district (Central Bohemia).

Allargentum, a natural hexagonal silver–antimony alloy of the composition AgSb, was described from the Rejzké pásmo Lode (Kutná Hora) by Kvaček and Novák (1972) as thin veinlets up to 1 mm thick in galena associated with Ag-rich tetrachloride, stannite and canfieldite.

Documented occurrences of gold or electrum (natural Au–Ag alloy) from Kutná Hora ore district were described by Trdlíčka and Hak (1962); however, the exact chemical composition was not known (emission spectral analysis only). Genetically closest (to Au-rich silver from Kutná Hora) samples of electrum from Nový Knín, Central Bohemia, range from Au22Ag78 to Au37Ag63 (Litochleb and Šrein 1995).

At smaller occurrences in vicinity of Kutná Hora and in the ore district itself, gold was occasionally detected in arsenopyrite in its invisible form (Staročeské pásmo and Turkaňské pásmo lodes, Malec 1997). The gold presence was proven chemically (Šrein et al. 2006). The finding of gold associated with pyrite and pyrrhotite at Malešov near Kutná Hora confirmed historical reports about gold panning in the Vrchlice stream (Šrein et al. 2006).

Therefore, the discovery of Au-rich silver in paragenesis with ullmannite and allargentum was surprising,
unexpected and so different from the known ore mineralization that it was decided to describe this occurrence in this short article.

2. Geological setting

Kutná Hora ore district is the second largest silver deposit on the territory of the Czech Republic (after Příbram) with two peaks of mining activity from the end of 13th century to the end of 16th century. The ore district covers the area of c. 10 × 5 km in N–S direction. It is a vein-type deposit of Variscan age. Ore veins are clustered in so-called ore zones or lodes (“pásmo” in Czech), each 1 to 3 km in length and 100–300 m in width.

The lodes are divided into two groups: 1) so-called “silver-rich” developed in gneisses of the variegated unit of the Kutná Hora Crystalline Complex in the southern part and “pyrite-rich” lodes in gneisses and migmatites of the Malín Unit in the northern part of the ore district (Holub et al. 1982).

The silver-rich assemblage consists mainly of miargyrite, pyrrargyrite, freibergite, galena, pyrite, sphalerite, berthierite and Pb–Sb (–Ag) sulphosalts (boulangerite, jamesonite and owyheeite) in quartz–kutnahorite gangue. The pyrite-rich assemblage comprises pyrite, arsenopyrite, sphalerite, Ag-bearing galena, pyrrhotite, marcasite, chalcopyrite, stannite, freibergite–tetrahedrite and Pb–Sb (–Ag) and Ag–Bi– Pb sulphosalts (Pažout 2017) in quartz gangue without kutnahorite.

Local bonanzas of silver minerals, such as allargentum, pyrrargyrite, argentite/acanthite, miargyrite, polybasite, stephanite, freibergite, diaforite and freieslebenite, without the presence of base sulphides, are characteristic of the Oselské pásmo and Roveňská pásmo “silver” lodes. Fragments of this gangue material were found by RP on the overgrown remnants of medieval mine dumps.

The history of mining on the Oselské pásmo Lode was described by Bílek (2000). This lode – together with the Staročeské pásmo Lode in the north – was the most important deposit of the ore district, both in terms of economy and extent of mining, with the depths of 500 m reached before the end of the 14th century.

3. Experimental techniques

Mineral analyses of two polished sections of the sample OS 4 were obtained using Cameca SX 100 electron probe microanalyzer at the Geological Institute of the Czech Academy of Sciences, Suchdol, Prague; the correction procedure X–φ was applied (Merlet 1994). The operating conditions were: the accelerating voltage 20 kV, beam current 20 nA and focused beam (diameter ~0.8 µm). The following standards and X-ray lines were used: marcasite (S Kα, Fe Kα), tugtupite (Cl Kα), sphalerite (Zn Kα), stibnite (Sb Lα), CdS (Cd Lα), galena (Pb Mα), Bi2Se3 (Se Lα), GaAs (As Lα), Mn (Mn Kα), Cu (Cu Kα) and Ag (Ag Lα).

Au-rich silver was analysed with the electron probe microanalyzer JEOL JXA-8530F housed at Institute of Petrology and Structural Geology, Faculty of Science, 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 (Au Lα), cuprite (Cu Kα), cinnabar (Hg Lα), Bi2Se3 (Se Lα), Ag (Ag Lα), Sb2Te3 (Te Lα), stibnite (Sb Lα) and marcasite (S Kα).

4. Results and discussion

As a part of the systematic research of Kutná Hora ore district by the present authors, two samples of ores from the Oselské pásmo Lode were investigated by wet chemical analysis on contents of gold and silver (unpublished data of V. Šrein). One of them (sample MU 6) consisted of breccia patches rich in fine-grained galena and chalcopyrite in hydrothermally altered limonitized gneiss resembling gossan ore type from the probably cementation mineralization of uppermost parts of the Oselské pásmo Lode sampled underground in the so-called Museum Mine. This sample yielded 5.5 g/t Au and 5000 g/t Ag. The other tested sample (OS 4) was by coincidence taken from the same sample (find), in which ullmanmite, allargentum and Au-rich silver was later identified. This sample showed 2 g/t Au.

A sample with the Ni–Sb–Ag–Au association represented by ullmanmite and Au-rich silver was discovered in 2001 on the dump of the medieval Hutrejtěře Mine in the southernmost part of the Oselské pásmo Lode, in vicinity of the Church of Holy Trinity. A large piece of gangue was formed by a block of sericitized gneiss with thin veinlets of calcite and quartz with disseminated grain aggregates of pyrrargyrite, freibergite, pyrite, galena and sphalerite. Fractures in veinlets contain small metallic outgrowths, platelets and irregular crystalline aggregates and grains of yellowish allargentum, locally covered by black coatings of acanthite and violet–brown aggregates of chlorargyrite. Individual aggregates measure up to 2 mm, accumulations of aggregates cover an area of 5 × 2 cm. Several polished sections were prepared from the sample and the subsequent study revealed the presence of ullmanmite, allargentum and Au-rich silver, which are the subject of this paper.

4.1. Ullmanmite, allargentum and freibergite

Ullmanmite was identified in two polished sections as subhedral grains up to 50 µm across associated with
allargentum. In Fig. 1 a subhedral grain of ullmannite forms a crystallization core on which subhedral freibergite grew and both minerals have been replaced by allargentum, which changes along the grain boundaries into acanthite. Chemical composition of the studied ullmannite (Tab. 1) is close to the ideal formula NiSbS with only trace amounts of As (to 0.81 wt. %); contents of all other measured elements (Ag, Mn, Fe, Cu, Zn, Se, Cl, Cd, Pb and Au) are below detection limits. The average chemical composition of ullmannite can be expressed on the basis of Ni + Sb + S = 3 \text{ apfu} as Ni$_{0.98}$Sb$_{1.01}$As$_{0.01}$S$_{1.00}$.

The allargentum forms irregular grain aggregates several hundred µm across replacing ullmannite. The results of chemical analyses (Tab. 2) correspond well to the ideal stoichiometry of allargentum formula Ag$_6$Sb. All other measured elements (S, Mn, Fe, Cu, Zn, Se, Cl, Cd, Pb and Ni and Au) are mostly below detection limits. The average chemical composition of allargentum can be expressed on the basis of 7 \text{ apfu} as Ag$_{5.97}$Sb$_{0.99}$.

The associated freibergite with 6.3 \text{ apfu} Ag and a formula (Ag$_{6.32}$Cu$_{3.82}$Fe$_{1.01}$Zn$_{0.43}$Sb$_{4.26}$S$_{12.42}$) shows a composition typical of freibergite from Kutná Hora (unpublished data of the authors).

\textbf{4.2. Au-rich silver and Au-bearing dyscrasite}

\textit{Au-rich silver} forms irregular grains up to 5 µm in a close contact with freibergite which is replaced by pyrargyrite.
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the youngest mineral (Fig. 2). The chemical composition of the analysed grain (Tab. 3) corresponds to Au-rich silver with the Au content 15.52–16.3, Ag 76.20–76.80 and Sb 2.54–3.48 wt. %. Other elements above the detection limits include Cu (0.10–0.14 wt. %, detection limit, DL, of 0.026 wt. %), Te (0.11–0.18 wt. %, DL 0.027 wt. %) and S (0.48–0.60 wt. %, DL 0.01 wt. %). Other measured elements (Se and Hg) were found to be below their respective detection limits. The measured sulphur is not considered to be part of the Au-rich silver alloy. Calculated to the total metal content of 100 apfu, the formula of Au-rich silver from Kutná Hora is \( \text{Au}_{9.7}\text{Ag}_{85.0}\text{Sb}_{2.9} \).

\( \text{Au-bearing dyscrasite} \) was found in one anhedral grain of 5 μm in calcite in the same polished section (OS 4) as Au-rich silver. The Au contents are 0.66 and 0.74 wt. % with the detection limit of 0.12 wt. %. Two measured compositions of this phase correspond to the empirical formula \( \text{Ag}_{0.05}\text{Au}_{0.02}\text{Sb}_{0.36} \) and \( \text{Ag}_{0.14}\text{Au}_{0.01}\text{Sb}_{0.31} \), respectively, showing a surplus of silver and a deficit of antimony (Tab. 2), a frequent feature of this mineral (Anthony et al. 1990).

A single analysis with a slightly increased Au content, corresponding to \( \text{Au-bearing allargentum} \), was obtained from a grain of c. 15 μm in calcite in the polished section OS 4 located between the Au-rich silver and Au-bearing dyscrasite grains. However, the obtained Au content of 0.24 wt. % is close to the detection limit of 0.11 wt. % and thus questionable. Attempts to obtain more analyses yielded a composition with 0.41 wt. % of Au (with DL 0.12 wt. %) and a good total of 100.63 %, but with 2.16 wt. % of sulphur (6.98 at. %) assumed to reflect a contamination from nearby phases. Interestingly, this grain of allargentum is in the same polished section as allargentum associated with uillmannite that is gold-free within experimental errors (zero or below detection limit). Taken together, allargentum is not considered to be a confirmed Au-bearing phase from the ore district.

### 4.3. Stephanite, pyrargyrite, miargyrite, acanthite

The same polished section gave an illustrative example of a “bonanza” of Ag-rich minerals of Kutná Hora “silver”

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**Fig. 2** Au-rich silver (Au, white) in a close contact with freibergite (F, medium grey). Freibergite is partly replaced by pyrargyrite (P, light grey). Back-scattered electron (BSE) image 40 μm wide.

**Fig. 3** Acanthite (A, light grey), stephanite (S, lighter medium grey), pyrargyrite (P, darker medium grey) and miargyrite (M, dark grey). Back-scattered electron (BSE) image 270 μm wide.

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**Tab. 3** Chemical composition of Au-rich silver (wt. % and at. %)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>1</th>
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<th>mean</th>
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<tr>
<td>Sb</td>
<td>3.48</td>
<td>2.89</td>
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<td>S</td>
<td>0.60</td>
<td>0.51</td>
<td>0.48</td>
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<tr>
<td>Total</td>
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<td>96.44</td>
<td>96.33</td>
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<tr>
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<td>85.36</td>
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<tr>
<td>Te</td>
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<td>0.13</td>
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<tr>
<td>Sb</td>
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<td>2.84</td>
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<td>S</td>
<td>2.23</td>
<td>1.88</td>
<td>1.81</td>
<td>1.97</td>
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Ullmannite and Au-rich silver from Kutná Hora

allargentum, dyscrasite, Au-rich silver, ullmannite and stephanite crystallized.

5. Discussion: the origin of Ni and Au

Serpentine bodies form an important part of the so-called Kutná Hora Crystalline Complex basement in the Kutná Hora area (Synek and Oliveriová 1993; Štědrá and Nahodilová 2009). Such bodies were encountered by boreholes in southern “silver” lodes both south of town as well as in its historic centre, including the Roveňské pásma and Oselské pásma lodes where medieval mining began. The cores from these boreholes are deposited in the Museum of Silver, Kutná Hora.

According to the latest research, these ultrabasic rocks contain as much as 2000 ppm of Ni (Šrein et al. 2006). The following nickel minerals have been identified in the Kutná Hora serpentinites: pentlandite, cobaltpentlandite, maucherite and millerite (Šrein et al 2007). Along with Ni, Au contents were determined, usually not exceeding 1 ppm. Gold was nevertheless confirmed in all samples even though the correlation between Ni and Au is weak (Šrein et al. 2007).

The source of gold was examined along with analogy with deposits from around the world, where gold was found in basic and ultrabasic rocks, e.g. in Pakistan (Miller and Loucks 1991). Given the frequency and proportions of the serpentinite bodies in the Kutná Hora area, the amounts of Au and Ni are significant. A part of gold may come from arsenopyrite of ore veins, in which Au contents exceeding 1 ppm were detected (Šrein et al. 2006).

Taken together, penetration of hydrothermal fluids could have caused the mobilization of nickel and gold from serpentinites and from earlier ore mineralization (arsenopyrite). This process is thought to have resulted in the breakdown of earlier (older) silver minerals while allargentum, dyscrasite, Au-rich silver, ullmannite and stephanite crystallized.

6. Conclusions

The discovery of ullmannite and natural Au-rich silver alloys (Au-rich silver and Au-bearing dyscrasite) in Kutná Hora ore district sheds new light on the elemental variability of this hydrothermal vein-type deposit of Variscan age. The source of nickel and gold was probably in the underlying serpentinitized ultrabasic bodies cut by the “silver” lodes in the South of the ore district. The serpentinites contain 2000 ppm of Ni and low but stable contents of Au. Penetration of the late-stage hydrothermal fluids could have caused the mobilization of Ni and Au from serpentinites and in earlier ore mineralization (arsenopyrite).

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References

KVÁČEK M, NOVÁK F (1972) Allargentum in the Kutná Hora ore-district. Čas Mineral Geol 17: 297–300

PÁŽOUT R (2017) Bi and Bi–Sb lillianite homologues from Kutná Hora ore district, Czech Republic: a case of large-scale Sb for Bi substitution. J Geosci 62: 37–57