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A world-unique association of staročeskéite, izoklakeite and terywallaceite from Kutná Hora ore district, Czech Republic

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Abstract

A very interesting and world-unique association of Ag-Pb-Bi-Sb sulfosalts staročeskéite, izoklakeite-giessenite and terywallaceite has been found and determined from the Staročeské pásmo Lode of the Kutná Hora ore district, Czech Republic. Associated mineral include Sb-rich gustavite, Sb-rich treasurite, holubite, *schirmerite* (type 2), Bi-rich jamesonite and Ag,Bi-rich galena. The studied mineral association includes sulfosalts constituted by both Bi and Sb (staročeskéite, terrywallaceite, izoklakeite, holubite) as well as Sb-rich varieties of Bi-lillianite homologues and Bi-rich varieties of Sb sulfosalts (Bi-rich jamesonite). Staročeskéite has the empirical formula based on 11 *apfu* $Ag_{0.72}Cu_{0.01}(Pb_{1.59}Fe_{0.02}Cd_{0.01})_{\Sigma 1.62}(Bi_{1.31}Sb_{1.44})_{\Sigma 1.75}S_{5.91}$, in a very good agreement with the ideal formula. The Bi-richest izoklakeite (Bi/(Sb + Bi) = 0.70) found so far anywhere in the world was determined among the compositions of minerals of the izoklakeite - giessenite series. The so far Bi-richest izoklakeite with Bi/(Sb + Bi) = 0.68 was reported from Otome mine, Japan. The observed succession trend progresses from the earliest Bi-richest minerals to youngest Sb-richest members, starting with Ag,Bi-rich galena and ending with Bi-rich jamesonite being the latest, in line with previously reported observations. Empirical formulas of main and associated minerals and degrees of substitutions are discussed.

Key words: *staročeskéite, terywallaceite, izoklakeite, Ag-Pb-Bi-Sb sulfosalts, chemical composition, associated minerals, Kutná Hora ore district, Czech Republic*

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Introduction

Staročeskéite, ideally $Ag_{0.70}Pb_{1.60}(Bi_{1.35}Sb_{1.35})_{2.70}S_6$, the ^4L homologue of the lillianite homologous series of minerals, was described by Pažout, Sejkora (2018) from the Staročeské pásmo Lode of the Kutná Hora ore district. The structure of the mineral was solved by Pažout, Dušek (2010), unlike all other lillianite homologues with N = 4 the mineral is orthorhombic and isostructural with lillianite. To the best knowledge of the author, this mineral has so far not been identified from any other locality around the world, not even from localities where other Bi-Sb sulfosalts of the lillianite homologous series with N = 4 were found and described such as Julcani, Peru, (terrywallaceite), Chocaya, Bolivia (oscarkempffite, clino-oscarkempffite) and Oruro, Bolivia (a possible lazerckerite) (Pažout et al. 2024) and Alyaskitovoe, Yakutia, Russia (Mozgova et al. 1988).

Terrywallaceite, $AgPb(Sb,Bi)_3S_6$, again the ^4L homologue of the lillianite homologous series, is isostructural with gustavite and can be generally classified as an Sb--rich gustavite with such a degree of the Sb for Bi substitution that antimony prevails in one of the three Bi sites in the structure of gustavite ($AgPbBi_3S_6$, an end-member of the gustavite-lillianite solid-solution series); which occurs at Bi/(Bi + Sb) = 0.75. The structure of Sb-rich gustavite with Bi/(Bi + Sb) = 0.70 (i.e. *de facto* terrywallaceite) was determined by Pažout, Dušek (2009) on a sample from Kutna Hora ore district, Czech Republic, and the mineral was described and named terrywallaceite by Yang et al. (2013) on a sample with Bi/(Bi + Sb) = 0.49 from Julcani, Peru.

Minerals of the izoklakeite - giessenite series are Ag,Cu- bearing Pb-Bi-Sb sulfosalts, known from about 15 localities around the world with the simplified formula $Cu_2Pb_{22}Ag_2(Bi,Sb)_{22}S_{57}$ (Moëlo et al. 1995). The compositional ranges for natural members of this series are as follows (*apfu*): Cu + Fe < 2 (range 1.81 - 2.14), Pb + 2Ag ~ 26 (25.72 - 27.67), Bi + Sb ~ 22 (20.90 - 23.18) (Mikuš et al. 2019; Števko, Sejkora 2021; Pažout et al. 2017). The symmetry of giessenite (Bi-rich) is monoclinic (Makovicky, Karup-Møller 1986) and that of izoklakeite (Sb-rich) is orthorhombic (Armbruster and Hummel 1987). The exact Sb/Bi ratio, at which the symmetry changes, is unknown. According to the current status (Moëlo et al. 1995; Ozawa et al. 1998), the name izoklakeite is applied to all samples with Sb/Bi atomic ratio close to 1 (i.e. Bi/(Bi + Sb) close to 0.50), even for samples with Bi > Sb. The Bi-richest izoklakeite found so far was identified from Otome mine, Japan (Ozawa et al. 1998) with Bi/(Sb + Bi) = 0.68 (27.15 wt.% Bi and 7.32 wt. % Sb), who measured the sample on the single-crystal diffractometer and did not find the reflections observed in the monoclinic giessenite.

Schirmerite (Type 2) is a specific mineral entity with the formula $Ag_3Pb_3Bi_9S_{18}$ to $Ag_3Pb_6Bi_7S_{18}$, but not an approved mineral species. Re-examination of *schirmerite* (Type 2) from the type deposit (Makovicky, Karup-Møller

1977) proved it to be a disordered intergrowth of different proportions of slabs ^{4}L and ^{7}L, with a composition between those of gustavite and Ag,Bi-rich heyrovskýite. Such a disordered intergrowth is not a valid species. Yet these compositions appear among analyses of lillianite homologues from more localities.

The description of an unusual association of the above sulfosalts and further associated minerals and their chemistry is the subject of this paper.

Sample and occurrence

The samples with staročeskéite, izoklakeite and terywallaceite were found among the medieval mine dump material collected by the author of the article in 2000 at a construction site in the area of Staročeské pásmo Lode of the Kutná Hora ore district. Earthwork for construction (housing, road, gas or water pipe systems) in the urban area of the municipality (village) of Kaňk is a valuable source of gangue material as the majority of the village lies directly on or above the vast medieval (ca. 1290 - 1590) mine dumps of this lode, partly in original shape.

The Kutná Hora Ag-Pb-Zn ore district (Central Bohemia, Czech Republic) is an example of the hydrothermal vein-type mineralization of Variscan age (Holub et al. 1982; Pažout 2017; Pažout el al. 2017), which shows many similarities with the Freiberg Ag-Pb-Zn district, Saxony, Germany (Swinkels et al 2021; Pažout et al. 2018).

The unique association of staročeskéite, izoklakeite and terywallaceite (sample ST4) was found as part of large (app. ten kilograms) fragment of coarse-grained, drusy, limonite-coloured quartz with lenses of pyrrhotite, chalcopyrite and minor marcasite and macroscopic silvery-grey aggregates of bismuth sulfosalts of the lillianite homologous series and izoklakeite up to 15 mm across, often intergrowing with pyrrhotite. No macroscopic galena and no pyrite are present in the gangue.

Methods of identification

Quantitative chemical analyses were performed with electron microprobe (EPMA) in the wave length-dispersive mode (WDS). The samples were measured on CAMECA SX100 electron probe microanalyser at the Na-

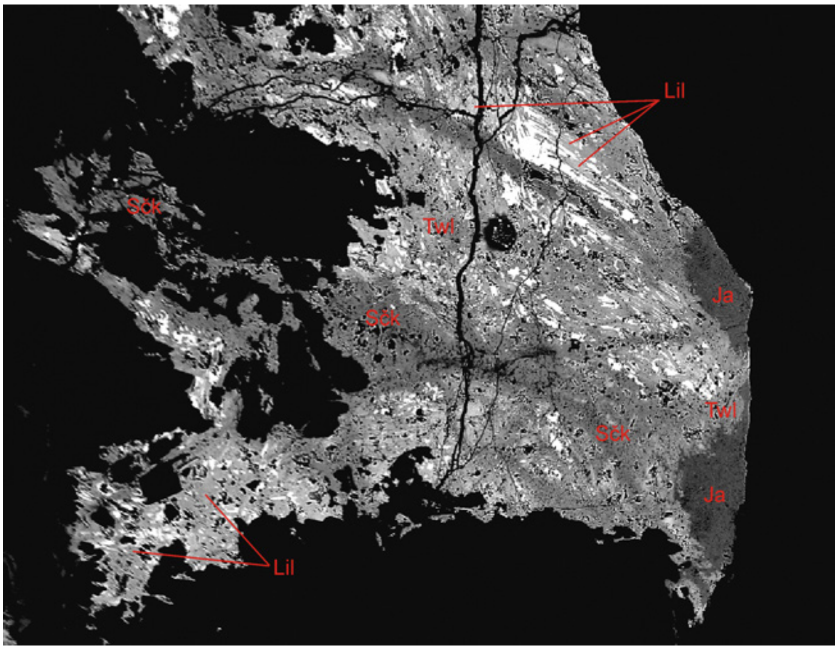

Fig. 1 *Veinlets and zones of staročeskéite (dark grey, Sčk) running horizontally parallel from left to right across the grain F1 are zonally changing into and replacing terrywallaceite (medium grey, Twl), which is replacing Bi-richer lillianite homologues (lighter medium grey, Lil): treasurite, gustavite, schirmerite (type 2). The oldest minerals in the grain are Ag,Bi-rich galena (white). The youngest mineral is Bi-rich jamesonite (two grains on the right edge of the grain, the darkest grey, Ja). BSE image (field of view 1000 μm).*

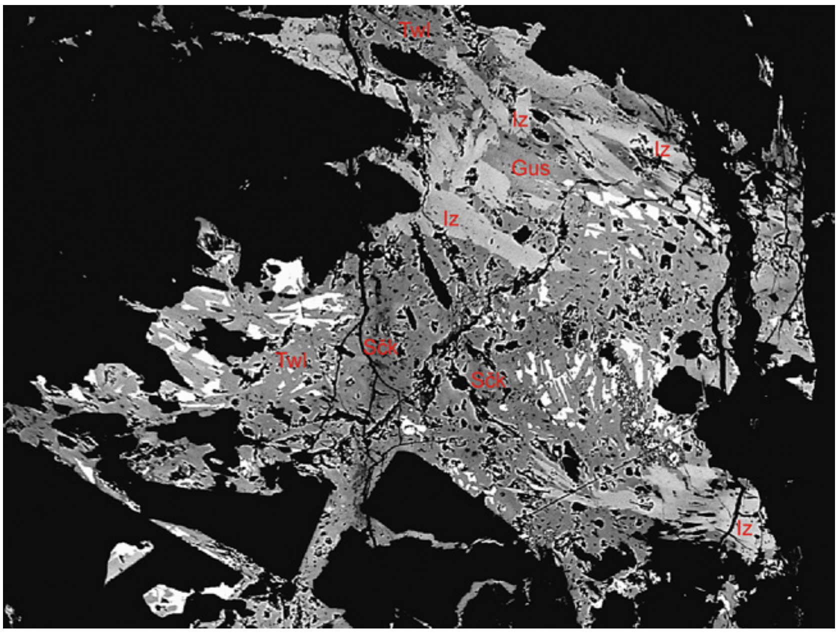

Fig. 2 *An association of staročeskéite (dark grey in the centre, Sčk), terrywallaceite (slightly lighter shade of grey, Twl), Sb-rich gustavite (even lighter, Gus), izoklakeite (light grey rectangular crystals, Iz) and Ag,Bi-rich galena (white) in the grain F5 of the sample ST 4 F, BSE image (field of view 600 μm).*

tional Museum, Prague. The analytical conditions were as follows: WDS mode, accelerating voltage of 25 kV, beam current of 20 nA, electron-beam diameter of 2 μm and standards: chalcopyrite (S*K*α), Bi_2Se_3 (Bi*M*β), PbS (Pb*M*α), Ag (Ag*L*α), halite (Cl*K*α), Sb_2S_3 (Sb*L*α), CdTe (Cd*L*α), HgTe (Hg*M*α), pyrite (Fe*K*α), Cu (Cu*K*α), ZnS (Zn*K*α), NiAs (As*L*β) and PbSe (Se*L*β). Measured data were corrected using PAP algorithm (Pouchou, Pichoir 1985).

Results

The unusual association of staročeskéite, izoklakeite and terrywallaceite was found in several grains of the polished section ST 4 F. All grains show a complex and complicated pattern of replacement processes. The grains are formed by an intergrowth of nine mineral species with observable trends of replacement of older Bi-richer minerals by younger Sb-richer phases. In the grain F1 (Fig. 1) the central part in the length of 650 μm from left to

Table 1 *Chemical composition of staročeskéite (sample ST 4 F) from Staročeské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu, N and L% for lillianite homologues)*

point	1775	1776	1778	1792	1798	1799	1801	1805	1815	1826	1828	1908	1925
Ag	7.48	7.30	7.57	7.21	7.30	7.01	6.82	7.50	7.27	8.09	7.29	7.58	7.49
Cu	0.13	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Pb	31.61	31.18	31.50	32.40	32.00	31.84	32.21	30.95	31.33	29.58	31.43	30.51	31.01
Fe	0.06	0.00	0.00	0.53	0.05	0.00	0.09	0.04	0.11	0.10	0.05	0.12	0.22
Cd	0.18	0.09	0.15	0.13	0.11	0.15	0.10	0.12	0.09	0.08	0.09	0.09	0.15
Mn	0.00	0.00	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.07	0.09	0.00	0.00	0.00	0.00	0.00	0.07	0.05	0.00	0.00	0.00	0.05
Sb	17.70	15.88	16.39	16.46	17.72	16.49	16.49	16.25	16.64	15.89	17.19	17.43	16.68
Bi	24.60	27.44	26.74	25.13	24.91	26.24	25.22	27.39	26.16	28.45	25.36	25.36	26.08
S	18.21	18.00	17.93	18.01	18.27	17.95	17.51	18.05	17.94	18.15	18.48	18.28	18.32
total	100.04	99.98	100.31	99.91	100.44	99.68	98.44	100.37	99.59	100.34	99.89	99.42	100.00
Ag	0.72	0.71	0.74	0.70	0.70	0.69	0.68	0.73	0.71	0.78	0.70	0.73	0.72
Cu	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Pb	1.58	1.59	1.60	1.63	1.60	1.62	1.67	1.57	1.59	1.49	1.57	1.53	1.56
Fe	0.01	0.00	0.00	0.10	0.01	0.00	0.02	0.01	0.02	0.02	0.01	0.02	0.04
Cd	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mn	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Sb	1.51	1.37	1.41	1.41	1.51	1.43	1.45	1.40	1.44	1.36	1.46	1.49	1.42
Bi	1.22	1.38	1.34	1.26	1.24	1.32	1.30	1.37	1.32	1.42	1.26	1.26	1.30
S	5.90	5.92	5.88	5.87	5.91	5.91	5.87	5.90	5.89	5.91	5.98	5.94	5.94
N	4.11	3.97	4.07	4.22	4.01	3.93	3.95	3.99	3.98	4.09	3.97	4.02	4.07
L	70.56	71.44	70.77	64.66	70.11	69.31	67.21	72.04	70.32	75.23	70.69	72.66	70.24
Bi/(Bi+Sb)	0.45	0.50	0.49	0.47	0.45	0.48	0.47	0.50	0.48	0.51	0.46	0.46	0.48

Chemical formulae were calculated on the basis 11 S atoms. The chemical homologue numbers N and L% were calculated after Makovicky, Karup-Moller (1977).

Table 2 *Chemical composition of izoklakeite (sample ST 4 F) from Staročeské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu)*

point	1858	1859	1857	1856	1819	1869	1820	1868	1847	1821	1849	1872	1873
Ag	1.84	1.98	1.88	2.84	2.33	2.58	2.42	1.96	2.50	2.02	1.95	1.96	1.91
Cu	1.18	1.17	0.98	0.85	0.97	0.91	0.98	0.95	0.84	0.94	0.89	0.86	0.86
Pb	44.89	44.48	45.08	42.67	42.95	41.90	42.25	43.59	42.20	43.62	43.37	43.33	43.78
Fe	0.20	0.17	0.82	0.87	0.17	0.17	0.16	0.17	0.16	0.18	0.39	0.20	0.22
Sb	14.11	13.57	12.69	12.66	10.88	10.70	10.67	10.05	9.89	9.57	9.30	7.89	7.14
Bi	20.34	20.15	22.04	23.41	25.46	26.26	26.40	25.89	26.95	27.15	26.65	29.08	29.26
S	17.60	17.43	17.96	17.99	17.19	17.77	17.08	17.61	17.18	17.16	17.17	17.21	16.84
total	100.16	98.95	101.45	101.29	99.95	100.29	99.96	100.22	99.72	100.64	99.72	100.53	100.01
Ag	1.76	1.91	1.77	2.66	2.28	2.48	2.37	1.90	2.46	1.98	1.92	1.94	1.91
Cu	1.91	1.92	1.56	1.35	1.61	1.49	1.63	1.57	1.40	1.57	1.49	1.44	1.46
Pb	22.34	22.38	22.06	20.81	21.88	20.98	21.58	22.03	21.62	22.29	22.24	22.28	22.85
Fe	0.37	0.32	1.49	1.57	0.32	0.32	0.30	0.32	0.30	0.34	0.74	0.38	0.43
Sb	11.95	11.62	10.57	10.51	9.43	9.12	9.27	8.64	8.62	8.32	8.12	6.91	6.34
Bi	10.03	10.05	10.69	11.32	12.86	13.04	13.37	12.97	13.69	13.75	13.55	14.83	15.14
S	56.59	56.67	56.80	56.71	56.58	57.51	56.37	57.51	56.88	56.66	56.90	57.19	56.79
Bi/(Bi+Sb)	0.46	0.46	0.50	0.52	0.58	0.59	0.59	0.60	0.61	0.62	0.63	0.68	0.70

Empirical formulas were calculated on the basis of 105 *apfu*. Analyses are ordered according to the increasing Bi content.

right and width of 130 μm is formed by staročeskéite (dark grey) that replaces terrywallaceite (medium grey) and Sb--rich gustavite (a fraction lighter shade of grey than terrywallaceite). This grain represents a typical association of Bi-Sb sulfosalts in the sample ST 4 F with the succession galena (white) - izoklakeite (light grey) - *schirmerite* (type 2) (medium grey) - Sb-rich gustavite (medium grey) - terrywallaceite (darker medium grey) - staročeskéite (dark grey in the centre) - holubite (even darker) - Bi-rich jamesonite (the darkest grey on the right edge). In the grain F 5 (Fig. 2) staročeskéite forms a dark grey central part that replaces terrywallaceite and Sb-rich gustavite. Izoklakeite in this grain forms lamella-like aggregates and rectangular crystals that replace Ag,Bi-rich galena.

Staročeskéite has the empirical formula based on 11 *apfu* $Ag_{0.72}Cu_{0.01}(Pb_{1.59}Fe_{0.02}Cd_{0.01})_{\Sigma 1.62}(Bi_{1.31}Sb_{1.44})_{\Sigma 1.75}S_{5.91}$ (mean of thirteen analyses), in a very good agreement with the ideal formula. No elements other than those constituting the mineral (Ag, Pb, Bi, Sb and S) have been determined in amounts above 0.02 *apfu*. The average N of the lillianite homologue is 4.03, very close to ideal 4. The percentage of the lillianite-gustavite substitution (2 Pb^{2+} = Ag^{+} + Bi^{3+}) - L% - is 70.40, again practically identical with the ideal 70 %. The degree of Sb for Bi substitution Bi/(Bi + Sb) = 0.48, very close to ideal 0.50. The chemical composition of staročeskéite is in Table 1.

Minerals of the izoklakeite - giessenite series are represented by a): typical izoklakeite with Bi/(Bi + Sb) ranging 0.46 - 0.63 (i.e. even compositions with Bi > Sb are still izoklakeite) (Fig. 2); b) compositions with Bi/(Bi + Sb) = 0.68 - 0.70, which represent the Bi-richest izoklakeite found so far anywhere (Fig. 3). The previous leader was izoklakeite from the Otome mine, Japan (Ozawa et al. 1998) with Bi/(Sb + Bi) = 0.68 (27.15 wt.% Bi and 7.32 wt. % Sb). The Bi-richest composition in this article has Bi/(Bi + Sb) = 0.70 (29.26 wt.% Bi and 7.14 wt. % Sb - analysis point 1873). The Sb-richest compositions have Bi/(Bi + Sb) = 0.46 (20.34 wt.% Bi and 14.11 wt. % Sb - analysis point 1858). Izoklakeite has the empirical formula based on 105 *apfu* $Cu_{1.57}(Pb_{21.95}Fe_{0.55})_{\Sigma 22.50}Ag_{2.10}(Bi_{12.72}Sb_{9.19})_{\Sigma 21.91}S_{56.86}$ (mean of thirteen analyses) and average Bi/(Sb + Bi) = 0.58 (Table 2).

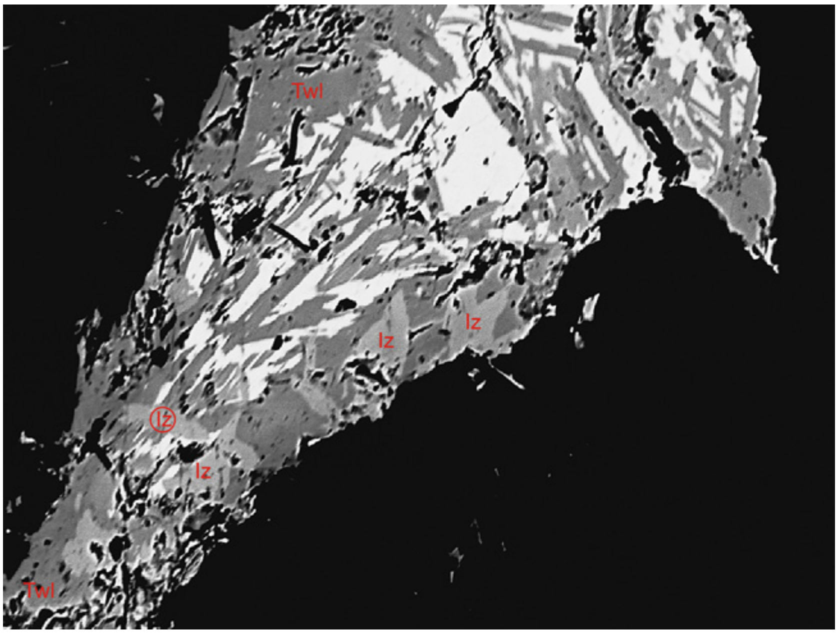

Fig. 3 *Izoklakeite (light grey, Iz) replacing Ag,Bi-rich galena (white), the oldest mineral in the association, and terywallaceite (darker grey, Twl) replacing izoklakeite. The lamella at the bottom left is the Bi-richest izoklakeite (Iz in circle) ever found anywhere, with the Bi/(Bi + Sb) = 0.70. Grain F8, BSE image (field of view 300 μm).*

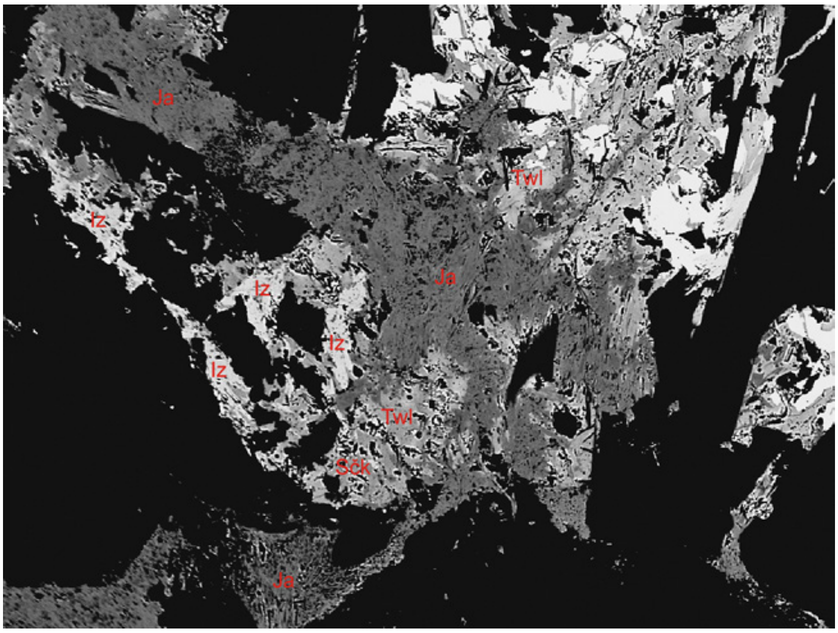

Fig. 4 *The typical character of replacement textures in the sample ST 4 F: the youngest dominating Bi-rich jamesonite (darkest grey, running across the image from top left and at the bottom left, Ja) replaces terrywallaceite (medium grey, Twl), staročeskéite (slightly darker medium grey, Sčk) and izoklakeite with Bi:Sb ~ 1:1 (light grey, Iz) above and below jamesonite, the oldest mineral is Ag,Bi--bearing galena (white). Grain F7, BSE image (field of view 600 μm).*

Terrywallaceite is present in all grains and it is the most frequent mineral in the described Ag-Bi mineralization. It mostly replaces earlier Bi-richer mineral phases, e.g. gustavite. The Sb-richest compositions have Bi/(Bi + Sb) = 0.56, corresponding to 1.29 *apfu* Sb (15.29 wt. %), the Bi-richest have Bi/(Bi + Sb) = 0.70, corresponding to 0.90 *apfu* Sb (10.34 wt. %). The N varies between 3.96 and 4.20, which is perfectly all right, and the substitution percentage L% of all analyses lies between 92.17 and 97.29 % (Table 3). Thus no oversubstituted terrywallaceite with L% around 105 - 106 or on the other hand with L% around 80 % (the lowest substitution limit known for terrywallaceite), both known from other terrywallaceite samples from Kutná Hora, were detected in this association. The empirical formula based on 11 *apfu* is $Ag_{0.98}Pb_{1.09}(Bi_{1.89}Sb_{1.05})_{\Sigma 2.94}S_{5.98}$ (mean of ten analyses). No minor elements apart from substantial Ag, Pb, Bi, Sb and S were found.

Gustavite in sample ST 4 F is in all analyses Sb-rich (Pažout et al. 2001), no Sb-free gustavite was detected. The empirical formula based on 11 *apfu* is $Ag_{0.99}Pb_{1.12}(Bi_{2.45}Sb_{0.52})_{\Sigma 2.97}S_{5.95}$ (mean of four analyses). No minor elements apart from Ag, Pb, Bi, Sb and S above the detection limit were found. The average N is 4.15, the substitution percentage L% = 93.19, and Bi/(Bi + Sb) = 0.82 (Table 4).

Schirmerite (Type 2) was detected in several compositions characterized by elevated values of N above 4, ranging from 4.51 to 4.75. The substitution percentage is between 76.64 and 82.43, and Bi/(Bi + Sb) = 0.80 - 0.82 (Table 4), well in line with previous analyses from Kutná Hora (Pažout 2017).

Table 3 *Chemical composition of terywallaceite (sample ST 4 F) from Staročeské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu, N and L% for lillianite homologues)*

point	1862	1863	1767	1844	1841	1842	1852	1840	1843	1839
Ag	10.42	10.04	9.78	10.19	10.16	9.95	9.85	10.28	10.10	9.97
Pb	21.58	21.29	22.80	21.64	21.81	21.33	21.58	21.25	21.15	20.93
Sb	15.29	15.11	14.06	12.75	11.48	11.52	10.80	10.74	10.80	10.34
Bi	33.90	34.37	34.93	37.42	38.69	39.22	38.95	39.75	40.06	40.48
S	18.77	18.62	18.19	18.39	18.12	18.34	18.22	18.21	18.19	18.18
total	99.96	99.43	99.76	100.39	100.26	100.36	99.40	100.23	100.30	99.90
Ag	0.99	0.96	0.95	0.98	0.99	0.97	0.97	1.00	0.99	0.98
Pb	1.07	1.06	1.15	1.09	1.11	1.08	1.10	1.08	1.08	1.07
Sb	1.29	1.28	1.21	1.09	0.99	0.99	0.94	0.93	0.93	0.90
Bi	1.66	1.70	1.75	1.86	1.95	1.97	1.97	2.00	2.02	2.05
S	6.00	6.00	5.93	5.96	5.95	5.99	6.01	5.98	5.98	5.99
N	4.12	3.96	4.08	4.12	4.20	4.03	4.14	4.20	4.12	4.11
L	95.73	97.29	92.17	94.51	93.08	95.67	93.62	94.54	95.38	95.38
Bi/(Bi+Sb)	0.56	0.57	0.59	0.63	0.66	0.66	0.68	0.68	0.68	0.70

Empirical formulas were calculated on the basis of 11 *apfu.* Analyses are ordered according to the increasing Bi content.

Table 4 *Chemical composition of associated minerals in the sample ST 4 F (Hol - holubite, Tre - treasurite, Gus - Sb-rich gustavite, Schir - schirmerite (type 2), Gal - Bi,Ag-rich galena, Jam - Bi-rich jamesonite) (wt. %, apfu, N and L% for lillianite homologues)*

point	1919	1818	1822	1823	1824	1768	1769	1766	1851	1855	1916
Mineral	Hol	Tre	Gus	Gus	Gus	Gus	Schir	Schir	Gal	Jam	Jam
Ag	7.83	7.34	9.69	9.50	9.51	9.80	9.20	8.98	0.79	0.08	0.02
Pb	30.69	35.59	20.24	21.78	21.13	20.91	24.67	26.75	84.19	37.84	37.23
Fe	0.23	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.02	2.44	2.37
Cd	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00
Sb	19.73	3.44	6.80	5.58	5.50	5.25	5.96	5.40	0.00	28.62	27.98
Bi	21.87	35.29	44.74	45.52	46.22	46.27	42.17	40.87	2.45	10.28	11.77
S	18.41	16.44	17.41	17.29	17.27	17.20	17.32	17.01	13.63	20.72	20.39
total	99.04	98.39	98.88	99.67	99.63	99.43	99.32	99.01	101.14	99.98	99.76
Ag	2.99	4.27	0.99	0.97	0.97	1.01	2.83	2.79	0.02	0.02	0.00
Pb	6.09	10.78	1.07	1.16	1.13	1.12	3.95	4.33	0.95	3.94	3.92
Fe	0.17	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.94	0.93
Cd	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb	6.67	1.77	0.61	0.51	0.50	0.48	1.62	1.49	0.00	5.07	5.02
Bi	4.31	10.60	2.35	2.40	2.44	2.45	6.69	6.57	0.03	1.06	1.23
S	23.62	32.18	5.97	5.95	5.95	5.94	17.90	17.81	1.00	13.95	13.88
N	4.12	5.87	4.09	4.22	4.14	4.26	4.51	4.78			
L	71.58	54.72	95.86	91.00	93.13	92.78	82.43	76.64			
Bi/(Bi+Sb)	0.39	0.86	0.79	0.83	0.83	0.84	0.80	0.82		0.17	0.20

Empirical formulas were calculated on the basis of n *apfu:* n = 44 for holubite, n = 60 for treasurite, n = 11 for gustavite, n = 33 for *schirmerite*, n = 2 for galena, n = 25 for jamesonite.

The detected treasurite (Table 4) is characterized by lower substitution L% of 54.72 (i.e. is Pb-richer and Ag--Bi-poorer), and is also Sb-rich, Bi/(Bi + Sb) = 0.82. The observed ranges of L% for treasurite from Kutná Hora are between 38.42 and 77.78 % and the Sb for Bi substitution between 0.81 and 0.95 (Pažout 2017).

Holubite was found as inclusions in a staročeskéite aggregate in the grain F1 (Fig. 1), its composition, characterized by N = 4.12, L% = 71.58 and Bi/(Bi + Sb) = 0.39 (Table 4), is close to the ideal composition of holubite (Pažout et al. 2023).

The earliest mineral in the described association is Ag,Bi-rich galena (Table 4), the latest mineral is Bi-rich jamesonite (Fig. 1, Fig. 4) with a significant $BiSb_{-1}$ substitution with Bi/(Bi + Sb) = 0.17 - 0.20 (up to 11.77 wt. % of Bi).

The observed general succession of the association in sample ST 4 F is: Ag,Bi-rich galena - izoklakeite - treasurite - *schirmerite* (type 2) - Sb-rich gustavite - terrywallaceite - staročeskéite - holubite - Bi-rich jamesonite, in line with previous observations.

Conclusions

A world-unique association of staročeskéite, izoklakeite and terywallaceite was determined in an ore sample from Staročeské pásmo Lode of the Kutná Hora ore district, Czech Republic. The detected suite of minerals include both the Bi-Sb sulfosalts constituted by both metals (staročeskéite, holubite, terrywallaceite, izoklakeite) as well as Sb-rich varieties of Bi-lillianite homologues (gustavite, treasurite, *schirmerite* (type 2)) and Bi-rich varieties of Pb-Sb sulfosalts (Bi-rich jamesonite). Thus the described Ag-Bi mineralization is formed mostly by minerals of the lillianite homologous series. The Bi-richest izoklakeite found so far anywhere in the world was determined among compositions of izoklakeite.

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