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PŮVODNÍ PRÁCE/ORIGINAL PAPER

Iron-bearing dantopaite from Kutná Hora ore district, Czech Republic, and its mineral association

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Abstract

Dantopaite, a very rare sulfosalt of Ag-Bi(-Pb-Cu), has been found and identified in samples from Staročeské pásmo Lode of the historic Ag-Pb-Zn Kutná Hora ore district, Czech Republic. Dantopaite, ideally $Ag_5Bi_{13}S_{22}$, is the only mineral of the pavonite homologous series found in the Kutná Hora ore district and it is the first occurrence of this rare sulfosalt in Czech Republic. It was determined in four grains of two samples of massive sulfide ores consisting of arsenopyrite, pyrrhotite and chalcopyrite with no presence of Ag-Bi lillianite homologues, typical of the Ag-Bi mineralization of the deposit. Each analysed grain represents a different dantopaite composition with regard to the Ag + Bi = 2 Pb substitution. The empirical formulas range from Ag,Bi-richest composition of $Ag_{3.62}Cu_{0.25}(Pb_{0.59}Fe_{1.07}Cd_{0.03})_{\Sigma 1.69}(Bi_{12.02}Sb_{0.23})_{\Sigma 12.25}S_{22}$ to the Pb-richest composition of $Ag_{3.18}Cu_{0.17}(Pb_{1.83}Fe_{1.30}Cd_{0.03}Mn_{0.05})_{\Sigma 3.21}(Bi_{11.71}Sb_{0.08})_{\Sigma 11.79}S_{22}$. A specific feature of this occurrence is the presence of iron in the chemical composition of this mineral, which is positively correlated with the lead content. The associated minerals include: a) minerals of the early sulfide stage (sphalerite, stannite) and cassiterite; b) minerals of the second sulfide stage: kenoargentotetrahedrite-(Fe) and minerals of the Ag-Bi mineralization (native bismuth, matildite, Ag,Bi-bearing galena, dantopaite; c) minerals of the latest Ag-Sb period (acanthite, stephanite). An overview of members of the pavonite homologous series is given.

***Key words**: dantopaite, pavonite homologue, Ag-Pb-Bi sulfosalts, chemical composition, Kutná Hora ore district, Czech Republic*

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Introduction

Dantopaite, ideally $Ag_5Bi_{13}S_{22}$, is the ^6P homologue of the pavonite homologous series of minerals. In this series of minerals the most common members are those with N = 5 (pavonite) and N = 7 (benjaminite). The order number of the homologue ^NP, could be explained as the number of octahedra in the PbS-like slab of the pavonite structure (Makovicky et al. 1977), where N is order number for the homologue and P is the name of the homologue series. Members of the pavonite homologous series are listed in Table 1.

Karup-Møller, Makovicky (1979) called the portion of copper fitting into the ideal formula of the pavonite homologues together with silver (i.e. occupying potentially the octahedral cation sites of the ideal structure) „substitutional copper“ (^sCu), the surplus copper they called „interstitial copper“ (^iCu). For the calculation of the order number N of a pavonite homologue analyzed by means of electron microprobe, Karup-Møller, Makovicky (1979) proposed to use three compromise formulae to help bracket the right and true value of N: calculation of the value called N_{P1}, in which all copper is taken to be ^iCu, N_{P2}, in which all copper is considered ^sCu and N_{P3}, for which copper is distributed equally between interstitial and substitutional modes.

The find of a hitherto unknown natural N = 6 member, dantopaite, in the Erzwies ore district, Gasteiner Valley, Austria, as late as in 2010 (Makovicky et al. 2010) reflects very specific conditions of the origin and an exceptional character of the occurrence. The associated sulfosalts at the type locality are lillianite-gustavite, heyrovskýite, eskimoite, vikingite, ourayite, bismuthinite, krupkaite, benjaminite, pavonite, and cosalite. It is a very rare mineral, apart from the type locality it is currently reported only from the Rozália mine (Slovakia) (Jeleň et al. 2012); the Clara mine (Germany) (Kolitsch et al. 2019), Yugo-Konevo deposit, Ural (Russia) (Kasatkin et al. 2023) and the Mohawk mine, Goldfield, USA (Musetti et al. 2024). Thus, Kutná Hora ore district, Central Bohemia, Czech Republic, is only the sixth occurrence of the mineral worldwide. The description of these finds and associated minerals is the subject of this paper.

Sample and occurrence

The samples with dantopaite were found in the material collected by the author in 2015 at the medieval dump of Kuntery Mine, one of the major medieval mines in the northern part of the Staročeské pásmo Lode of the Kutná Hora ore district (49.9777947° N, 15.2690425° E).

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). Geologically, mineralogically and petrologically, two mineral assemblages are present in this ore district, one „silver-rich” with larger accumulations of silver minerals in the southern part of the ore district and one „pyrite-rich” with the larger accumulations of Ag-bearing base sulfides in the northern part (Malec, Pauliš 1997). In the

Kutná Hora ore district, sulfide mineralization is rich in sulfosalts of Ag-Sb, Ag-Pb-Sb and Pb-Sb (Pažout et al. 2019) in both parts of the ore district, as well as sulfosalts of Ag-Pb-Bi, Ag-Pb-Bi-Sb and Pb-Bi-Sb in the northern part. The most frequent minerals in the Ag-Bi mineralization are sulfosalts of the lillianite homologous series (Pažout 2017; Pažout et al. 2017).

The Staročeské pásmo Lode is the biggest „pyrite-rich“ lode of the ore district. It is about 2.6 km long and several hundred meters wide and was extensively mined

Table 1 *Members of the pavonite homologous series*

Mineral	Chemical formula	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	s.g.	Ref.
N = 3							
Grumiplucite	$HgBi_2S_4$	14.17	4.05	13.98	118.3	*C*2/*m*	[1]
Kudriavite	$CdBi_2S_4$	13.10	4.00	14.71	115.6	*C*2/*m*	[2]
Graţianite	$MnBi_2S_4$	12.68	3.91	14.76	115.3	*C*2/*m*	[3]
N = 4							
Makovickyite	$Cu_{1.12}Ag_{0.81}Pb_{0.27}Bi_{5.35}S_9$	13.24	4.05	14.67	99.4	*C*2/*m*	[4]
Cupromakovickyite	$Cu_8Ag_2Pb_4Bi_{18}S_{36}$	13.40	4.02	29.95	100.0	*C*2/*m*	[4]
N = 4.5							
Cupromakopavonite	$Cu_8Ag_3Pb_4Bi_{19}S_{38}$	13.38	4.00	31.08	93.1	*C*2/*m*	[5]
N = 5							
Pavonite	$Ag_4Bi_{12}S_{20}$	13.30	4.04	16.42	94.0	*C*2/*m*	[6]
Cupropavonite	$Cu_{0.9}Ag_{0.5}Pb_{0.6}Bi_{2.5}S_5$	13.36	4.01	32.78	93.4	*C*2/*m*	[7]
Luboržákite	Mn_2AsSbS_5	12.51	3.80	16.05	94.2	*C*2/*m*	[8]
N = 6							
Dantopaite	$Ag_5Bi_{13}S_{22}$	13.38	4.05	18.69	105.5	*C*2/*m*	[9]
N = 7							
Benjaminite	$Ag_3Bi_7S_{12}$	13.30	4.07	20.21	103.3	*C*2/*m*	[10]
N = 8							
Mummeite	$Cu_{0.58}Ag_{3.11}Pb_{1.10}Bi_{6.65}S_{13}$	13.47	4.06	21.63	92.9	*C*2/*m*	[11]

N = homologue order; s.g. = space group. [1] Merlino et al. (2013); [2] Balić-Žunić, Makovicky (2007); [3] Ciobanu et al. (2014) [4] Topa et al. (2008); [5] Topa et al. (2012); [6] Makovicky et al. (1977); [7] Mumme et al. (2015); [8] Kasatkin et al. (2020); [9] Makovicky et al. (2010); [10] Makovicky, Mumme (1979); [11] Karup-Møller, Makovicky (1992).

Table 2 *Chemical composition of dantopaite (sample ST 414 E2) from Staročeské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu)*

point	67	68	69	70	1 R	2 R	3 R	4 R	5 R
Ag	9.56	9.54	9.54	9.61	9.68	9.55	9.61	9.79	9.56
Cu	0.17	0.18	0.14	0.18	0.19	0.20	0.23	0.12	0.19
Pb	5.53	5.54	5.36	5.41	5.36	5.59	5.32	5.44	5.72
Fe	1.46	1.65	1.60	1.75	1.24	1.23	1.17	1.45	1.30
Cd	0.19	0.19	0.16	0.16	0.15	0.29	0.24	0.18	0.28
Mn	0.20	0.18	0.17	0.19					
Bi	63.19	63.27	63.06	63.13	65.36	65.08	64.28	64.31	65.38
Sb	0.19	0.21	0.21	0.21	0.20	0.14	0.19	0.22	0.15
S	18.20	18.19	18.10	18.15	17.69	17.73	17.78	17.74	17.75
total	98.69	98.95	98.34	98.79	99.87	99.81	98.82	99.25	100.33
Ag	3.44	3.43	3.45	3.46	3.58	3.52	3.53	3.61	3.52
Cu	0.10	0.11	0.09	0.11	0.12	0.13	0.14	0.08	0.12
Pb	1.03	1.04	1.01	1.01	1.03	1.07	1.02	1.04	1.10
Fe	1.01	1.15	1.12	1.22	0.89	0.88	0.83	1.03	0.93
Cd	0.07	0.07	0.06	0.06	0.05	0.10	0.08	0.06	0.10
Mn	0.14	0.13	0.12	0.13					
Bi	11.72	11.74	11.76	11.74	12.47	12.39	12.20	12.24	12.43
Sb	0.06	0.07	0.07	0.07	0.07	0.05	0.06	0.07	0.05
S	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
N_{p1}	5.73	5.79	5.76	5.87	5.44	5.46	5.49	5.71	5.48
N_{p2}	5.77	5.84	5.80	5.92	5.49	5.51	5.56	5.74	5.53
N_{p3}	5.75	5.82	5.78	5.89	5.46	5.49	5.52	5.72	5.50

Chemical formulae were calculated on the basis of 22 S atoms. The chemical homologue numbers N_{p1}. N_{p2}. N_{p3} were calculated after Karup-Møller, Makovicky (1979) (see text). Points marked R were re-measured at 15 kV.

since the beginning of the 14th century soon after the discovery of the deposit. The lode is formed by two principal veins, the main Hlavní žíla Vein and the Benátecká žíla Vein, as well as several other veins such as Špitálská žíla Vein, Čížkovská žíla Vein and Mlynářská žíla Vein, reaching maximum thickness of the vein of 2 - 4 m and depths around 450 m (Holub 2018). Typical of this lode were huge reserves of massive sulfide ores formed by base metal sulfides, often silver-bearing, on the one hand and lower amounts of richer accumulations of silver minerals in the extracted ore on the other hand.

Dantopaite was found in four grains of two different finds (samples) (ST 414 and ST 413) in large blocks (several tens of kilograms) of massive sulfide ore deposited at the foot of the medieval dump of Kuntery Mine during the prospective survey mining of the near Benátecká žíla Vein of the Staročeské pásmo Lode in the 1960´s. This vein has a specific position in the ore district because it was discovered only in 1566, some 250 to 300 years after the discovery of the Hlavní žíla Vein (the Main Vein), the biggest vein of this Lode and of the whole ore district.

The sulfide ore is formed by massive base metal sulfides of the Fe-Zn-Cu-Sn-As mineralization of the first sulfide stage. Prevailing is arsenopyrite, pyrrhotite and chalcopyrite, less abundant are sphalerite and stannite. No macroscopic galena or pyrite and marcasite are present in the sulfide ore. The large fragments did not disintegrate but survive decades of exposure to weather, as a result of which they were covered by hard crusts of iron oxides/hydroxides on the surface but were intact underneath.

Both fragments are massive sulfide ore of the Fe-Zn-Cu-Sn-As mineralization. The Ag-Pb-Bi-Sb sulfosalts

Fig 1 *A grain of dantopaite (grey) and native bismuth (white) in arsenopyrite (black). Field of view 75 µm. BSE image of polished section ST 414 E2.*

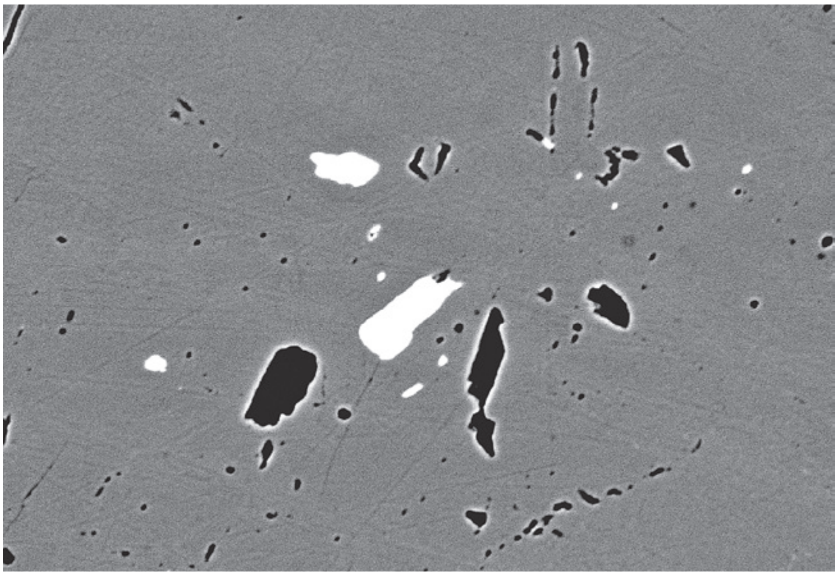

Fig 2 *Two grains of dantopaite (white) in arsenopyrite (points 1, 4, 5, 6, 9 - lower grain F3a; points 2, 3, 7, 8 - upper grain F3b). Field of view 200 µm. BSE image of polished section ST 413 B3.*

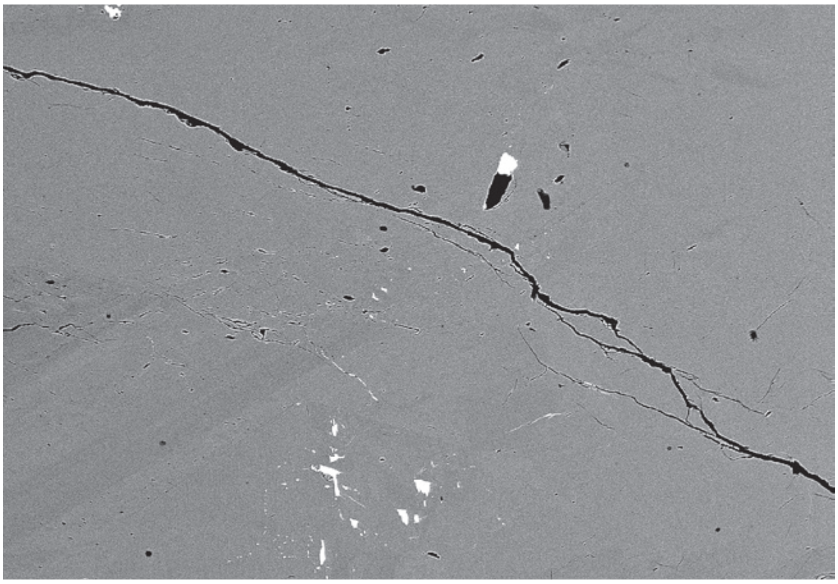

Fig 3 *An association of minerals occurring in arsenopyrite (dark grey): dantopaite (the upper central grain F4 above the crack, white), native bismuth (all grains bottom, white) and cassiterite (top left grain above the cracks, white). Field of view 1100 µm. BSE image of sample ST 413 B3.*

Table 3 *Chemical composition of dantopaite (grain F3a of sample ST 413 B3) from Staročeské pásmo Lode of Kutná Hora ore district. Czech Republic (wt. %, apfu)*

point	1	4	5	6	9	11 R	12 R	13 R	14 R	15 R
Ag	8.68	8.43	8.48	8.52	8.58	8.46	8.25	8.31	8.18	8.32
Cu	0.22	0.29	0.25	0.27	0.28	0.23	0.25	0.24	0.22	0.22
Pb	9.42	9.37	9.60	9.57	9.18	9.46	9.84	9.28	9.54	9.19
Fe	1.81	1.85	1.78	1.78	1.83	1.37	1.41	1.52	1.62	1.77
Cd	0.09	0.09	0.10	0.09	0.09	0.00	0.16	0.16	0.00	0.18
Mn	0.07	0.08	0.06	0.06	0.09					
Bi	60.67	60.66	60.97	60.85	60.96	63.32	60.69	61.10	62.27	61.79
Sb	0.23	0.24	0.27	0.25	0.23	0.24	0.24	0.22	0.26	0.27
S	17.32	17.55	17.55	17.56	17.71	17.53	17.51	17.35	17.42	17.46
total	98.51	98.56	99.06	98.95	98.95	100.61	98.35	98.18	99.51	99.20
Ag	3.28	3.14	3.16	3.17	3.17	3.16	3.08	3.13	3.07	3.12
Cu	0.14	0.18	0.16	0.17	0.18	0.15	0.16	0.15	0.14	0.14
Pb	1.85	1.82	1.86	1.86	1.76	1.84	1.91	1.82	1.86	1.79
Fe	1.32	1.33	1.28	1.28	1.31	0.99	1.02	1.11	1.17	1.28
Cd	0.03	0.03	0.04	0.03	0.03	0.00	0.06	0.06	0.01	0.06
Mn	0.05	0.06	0.04	0.04	0.07					
Bi	11.82	11.67	11.73	11.70	11.62	12.19	11.70	11.89	12.07	11.95
Sb	0.08	0.08	0.09	0.08	0.08	0.08	0.08	0.07	0.09	0.09
S	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
N_{p1}	6.14	6.01	5.99	6.03	6.03	5.52	5.78	5.75	5.60	5.78
N_{p2}	6.20	6.09	6.06	6.10	6.10	5.58	5.85	5.82	5.66	5.84
N_{p3}	6.17	6.05	6.03	6.07	6.07	5.55	5.82	5.79	5.63	5.81

Chemical formulae were calculated on the basis of 22 S atoms. The chemical homologue numbers N_{p1}. N_{p2}. N_{p3} were calculated after Karup-Møller, Makovicky (1979) (see text). Points marked R were re-measured at 15 kV.

Table 4 *Chemical composition of dantopaite (grain F3b of sample ST 413 B3) from Staročeské pásmo Lode of Kutná Hora ore district. Czech Republic (wt. %, apfu)*

point	2	3	7	8
Ag	9.16	9.17	9.01	9.10
Cu	0.16	0.18	0.20	0.18
Pb	6.91	7.12	6.81	7.16
Fe	2.03	2.05	1.99	2.22
Cd	0.13	0.11	0.07	0.11
Bi	62.68	62.44	62.06	62.23
Sb	0.19	0.21	0.21	0.22
S	17.74	17.66	17.82	17.84
total	99.04	98.99	98.22	99.12
Ag	3.38	3.40	3.31	3.34
Cu	0.10	0.11	0.12	0.11
Pb	1.33	1.37	1.30	1.37
Fe	1.45	1.47	1.41	1.57
Cd	0.05	0.04	0.02	0.04
Bi	11.93	11.93	11.76	11.77
Sb	0.06	0.07	0.07	0.07
S	22.00	22.00	22.00	22.00
N_{p1}	5.98	6.04	5.92	6.10
N_{p2}	6.02	6.09	5.97	6.15
N_{p3}	6.00	6.06	5.95	6.13

Chemical formulae were calculated on the basis of 22 S atoms. The chemical homologue numbers N_{p1}. N_{p2}. N_{p3} were calculated after Karup-Møller, Makovicky (1979) (see text).

of the lillianite homologous series, typical of the Ag-Bi mineralization found in the ore district - gustavite, terrywallaceite, lillianite, vikingite, treasurite, eskimoite, Ag,Bi-rich heyrovskýite, (Pažout 2017), staročeskéite (Pažout, Sejkora 2018), holubite (Pažout et al. 2023), lazerckerite (Pažout et al. 2024) - were not found in the association with dantopaite. Conversely, neither dantopaite, nor any other pavonite homologue have so far been identified among plentiful samples of the above-mentioned Ag-Bi mineralization with lillianite homologues. Another peculiarity is the fact that no other, more common pavonite homologues, such as pavonite and benjaminite, have so far been identified in the ore district.

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 National 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*α) and PbSe (Se*L*β). Measured data were corrected using PAP algorithm (Pouchou, Pichoir 1985).

Dantopaite was re-measured at lower accelerating voltage to examine whether the Fe content comes from adjacent arsenopyrite or indeed from dantopaite under the following conditions: 15 kV, 10 nA; the same standards and X-ray lines were used.

Results

Dantopaite

Dantopaite was found as four different grains. The first grain was identified in the polished section of sample ST 414 E2, and three grains in sample ST 413 B3. Each of the four grains differ in Pb content and as a result of Ag + Bi = 2 Pb substitution also in Ag and Bi contents. Results of electron-microprobe analyses for each of the four grains are presented in separate Tables 2 to 5.

The aggregate with dantopaite in the sample ST 414 E2 (Fig. 1) is an anhedral grain *app.* 35 × 10 μm in arsenopyrite. The right part of the aggregates is formed by dantopaite (points 68 - 70 in Table 2), the left part of the grain is native bismuth (pt. 71 in Table 6), most probably being replaced by dantopaite. Dantopaite has the average (mean of five analyses) Pb content of 1.02 *apfu* (5.46 wt. %) and the empirical formula $Ag_{3.44}Cu_{0.10}(Pb_{1.02}Fe_{1.12}Cd_{0.06}Mn_{0.13})_{\Sigma 2.34}(Bi_{11.74}Sb_{0.07})_{\Sigma 11.84}S_{22}$. Copper, often significantly present in pavonite homologues at other localites is very low (up to 0.13 *apfu*, i.e. 0.19 wt. %). Minor contents of Mn (up to 0.14 *apfu*) and Cd (up to 0.07 *apfu*) were also detected. The Sb content of 0.07 *apfu* (mean of five analyses) is in line with previous observations that antimony does not significantly substitute for bismuth in pavonite homologues. The substitution $SbBi_{-1}$, very frequent and nearly limitless in Ag-Bi sulfosalts of the lillianite homologous series from Kutná Hora ore district (Pažout 2017), is in the case of dantopaite practically absent. This is assumed to be related to the difficulty of pavonite homologues

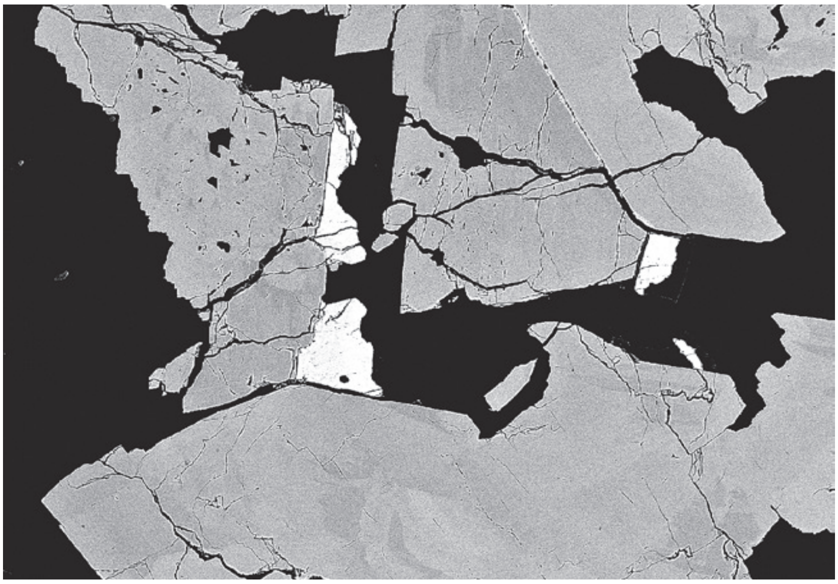

Fig 4 *The zonal arsenopyrite of sample ST 414 E2. Brighter shades of grey correspond to relatively stoichiometric arsenopyrite, darker shades of grey represent As-poor arsenopyrite. Stannite (white, pts 57, 58) is also present. Field of view 1100 μm. BSE image of sample ST 414 E2.*

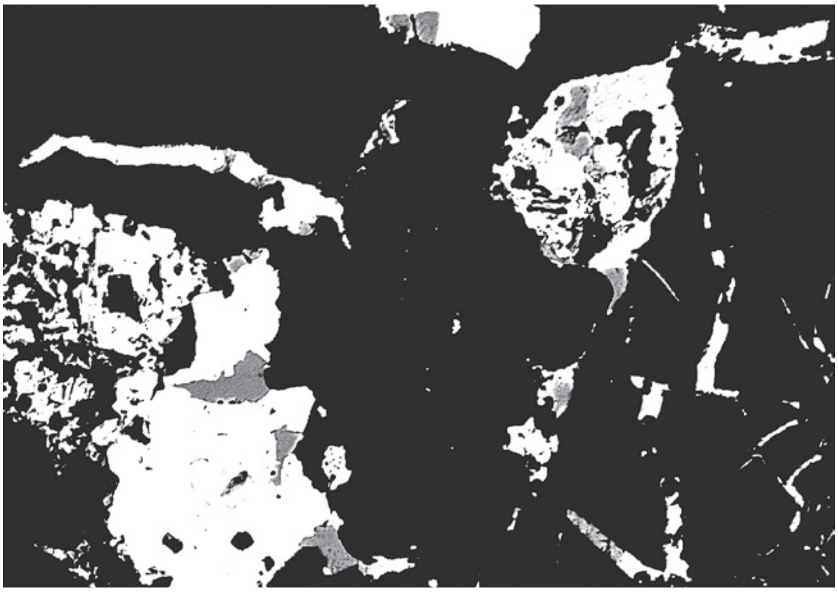

Fig 5 *Grains of Ag,Bi-rich galena (white) in arsenopyrite (black). Galena in the left grain is replaced by kenoargentotetrahedrite--(Fe) (medium grey, detail in Fig 6), in the right top grain galena is replaced by stephanite (grey). Field of view 350 μm. BSE image of sample ST 414 E2.*

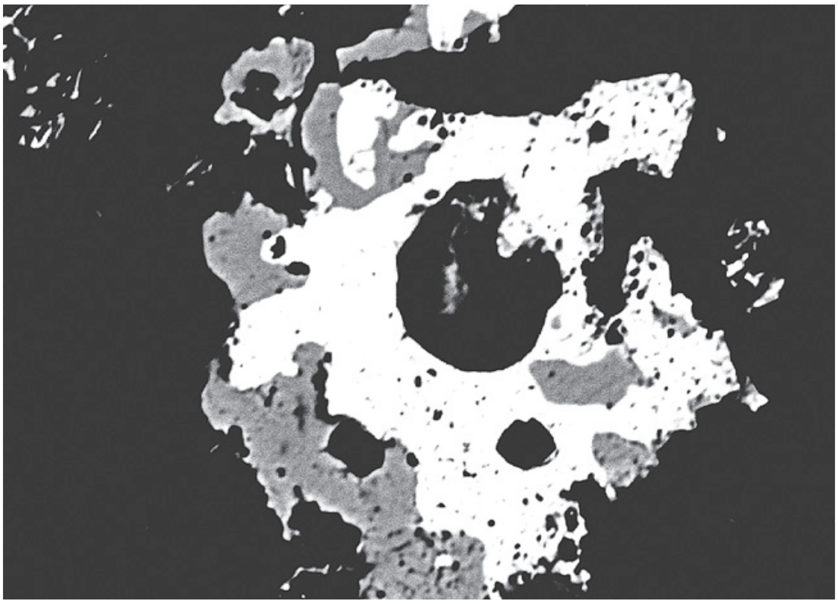

Fig 6 *Native bismuth (white, pt. 75) and Ag,Bi-rich galena (grey, pt. 76) in kenoargentotetrahedrite-(-Fe) (black, points 73, 74). Field of view 160 μm. BSE image of sample ST 414 E2 (a cut-out of bottom left area of Figure 5).*

Table 5 *Chemical composition of dantopaite (grain F4 of sample ST 413 B3) from Staročeské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu)*

point	15	13	14	10	11	12	6 R	7 R	8 R	9 R	10 R
Ag	10.09	9.92	9.73	9.92	10.13	9.99	10.16	10.37	9.96	10.36	10.04
Cu	0.38	0.37	0.40	0.47	0.38	0.39	0.31	0.21	0.21	0.31	0.35
Pb	3.38	3.05	3.10	2.97	3.02	3.24	3.21	3.09	3.14	3.41	2.94
Fe	2.07	1.51	1.49	1.39	1.36	1.33	1.33	1.29	1.28	1.12	1.46
Cd	0.09	0.08	0.09	0.04	0.10	0.06	0.12	0.07	0.00	0.07	0.00
Bi	63.61	63.89	64.67	64.45	64.21	63.79	64.77	66.01	65.98	64.45	64.81
Sb	0.72	0.69	0.70	0.71	0.72	0.76	0.70	0.72	0.73	0.67	0.72
S	17.85	17.92	18.15	18.03	18.12	17.94	17.83	17.88	17.88	17.88	18.05
total	98.21	97.46	98.34	97.98	98.07	97.54	98.43	99.64	99.18	98.27	98.37
Ag	3.70	3.62	3.51	3.60	3.66	3.64	3.73	3.79	3.64	3.79	3.64
Cu	0.24	0.23	0.24	0.29	0.23	0.24	0.19	0.13	0.13	0.19	0.22
Pb	0.64	0.58	0.58	0.56	0.57	0.61	0.61	0.59	0.60	0.65	0.55
Fe	1.46	1.06	1.04	0.97	0.95	0.94	0.94	0.91	0.90	0.79	1.02
Cd	0.03	0.03	0.03	0.01	0.03	0.02	0.04	0.02	0.01	0.02	0.01
Bi	12.03	12.03	12.03	12.07	11.96	12.00	12.26	12.46	12.46	12.17	12.12
Sb	0.23	0.22	0.22	0.23	0.23	0.25	0.23	0.23	0.24	0.22	0.23
S	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
N_{p1}	5.86	5.45	5.27	5.32	5.45	5.42	5.43	5.37	5.16	5.49	5.37
N_{p2}	5.96	5.55	5.38	5.45	5.56	5.53	5.52	5.43	5.22	5.58	5.46
N_{p3}	5.91	5.50	5.33	5.38	5.51	5.47	5.47	5.40	5.19	5.53	5.42

Chemical formulae were calculated on the basis of 22 S atoms. The chemical homologue numbers N_{p1}. N_{p2}. N_{p3} were calculated after Karup-Møller, Makovicky (1979) (see text). Points marked R were re-measured at 15 kV.

Table 6 *Chemical composition of associated minerals in sample ST 414 E2 (Stn - In-rich stannite, Apyl and Apyd - arsenopyrite bright and dark, Gn - Bi,Ag-rich galena, Bi - native bismuth, Ttr - kenoargentotetrahedrite-(Fe), Sph - stephanite)*

point	57	58	61	62	63	64	71	72	73	74	75	76	112	113
mineral	Stn	Stn	Apyl	Apyl	Apyd	Apyd	Bi	Ttr	Ttr	Ttr	Bi	Gn	Sph	Sph
Ag	0.10	0.13	0.00	0.00	0.00	0.00	0.00	33.94	34.01	34.35	0.00	1.44	66.47	67.71
Cu	28.62	28.49	0.02	0.03	0.03	0.01	0.00	13.52	13.36	13.47	0.01	0.02	0.06	0.06
Pb	0.08	0.00	0.07	0.16	0.12	0.10	0.00	0.00	0.07	0.07	0.00	81.99	0.07	0.00
Fe	11.71	11.82	34.66	34.76	35.16	35.36	0.97	5.54	5.38	5.23	0.00	0.19	0.28	0.22
Zn	2.32	1.98	0.00	0.00	0.00	0.00	0.00	0.63	0.68	0.65	0.00	0.00	0.00	0.00
In	0.18	0.33	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.05	0.00	0.00	0.00
Sn	27.32	27.34	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.04	0.00	0.00	0.00	0.00
Sb	0.00	0.00	0.00	0.08	0.00	0.00	0.00	26.14	26.44	26.39	0.06	0.00	14.08	14.60
Bi	0.00	0.00	0.00	0.00	0.00	0.00	98.44	0.00	0.00	0.00	99.16	3.12	0.00	0.00
As	0.00	0.00	44.65	44.12	41.07	41.02	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.17
S	29.55	29.72	20.70	21.08	23.07	23.00	0.01	20.66	20.32	20.23	0.00	14.06	14.49	14.92
total	99.88	99.81	100.10	100.23	99.45	99.49	99.51	100.43	100.32	100.43	99.28	100.82	95.60	97.68
Ag	0.000	0.010	0.000	0.000	0.000	0.000	0.000	6.100	6.160	6.230	0.000	0.030	5.170	5.140
Cu	1.950	1.940	0.000	0.000	0.000	0.000	0.000	4.120	4.110	4.150	0.030	0.000	0.010	0.010
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.010	0.000	0.910	0.000	0.000
Fe	0.910	0.910	1.000	1.000	0.990	1.000	3.550	1.920	1.880	1.830	0.000	0.010	0.040	0.030
Zn	0.150	0.130	0.000	0.000	0.000	0.000	0.000	0.190	0.200	0.190	0.030	0.000	0.000	0.000
In	0.010	0.010	0.000	0.000	0.000	0.000	0.160	0.000	0.000	0.000	0.090	0.000	0.000	0.000
Sn	0.990	0.990	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.010	0.000	0.000	0.000	0.000
Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.050	4.160	4.240	4.240	0.100	0.000	0.970	0.980
Bi	0.000	0.000	0.000	0.000	0.000	0.000	96.140	0.000	0.010	0.000	99.660	0.030	0.000	0.000
As	0.000	0.000	0.960	0.940	0.870	0.860	0.000	0.000	0.000	0.000	0.000	0.000	0.020	0.020
S	3.980	4.000	1.040	1.050	1.140	1.130	0.060	12.490	12.380	12.340	0.000	1.010	3.790	3.810

Empirical formulas were calculated on the basis of n *apfu*; n = 8 for stannite, n = 3 for arsenopyrite, n = 29 for kenoargentotetrahedrite-(Fe), n = 2 for galena, n = 10 for stephanite.

structures to accommodate antimony. Unlike structures of lillianite homologues with N = 4, in which - especially in the case of Kutná Hora ore district - antimony readily substitutes for bismuth and vice versa.

The dantopaite grain F3a in the sample ST 413 B3 (the lower white one in Fig. 2) is subhedral with dimensions of *app*. 30 × 10 µm in arsenopyrite. This grain (points 1, 4 - 6, 9 in Table 3) has the highest Pb content of all four grains (up to 1.86 *apfu*, i.e. 9.60 wt. %) and the empirical formula (mean of five analyses) $Ag_{3.18}Cu_{0.17}(Pb_{1.83}Fe_{1.30}Cd_{0.03}Mn_{0.05})_{\Sigma 3.21}(Bi_{11.71}Sb_{0.08})_{\Sigma 11.79}S_{22}$. The copper contents do not exceed 0.18 *apfu*. Minor contents of Mn (up to 0.07 *apfu*), Cd (up to 0.03 *apfu*) and Sb (up to 0.09 *apfu*) were also detected.

The dantopaite grain F3b in the sample ST 413 B3 (the upper white one in Fig. 2) is an anhedral grain with dimensions of *app.* 18 × 8 µm in arsenopyrite. This grain (points 2, 3, 7, 8 in Table 4) has Pb contents up to 1.37 *apfu* (7.16 wt. %), and the empirical formula (mean of four analyses) $Ag_{3.35}Cu_{0.11}(Pb_{1.34}Fe_{1.47}Cd_{0.04})_{\Sigma 2.85}(Bi_{11.85}Sb_{0.07})_{\Sigma 11.92}S_{22}$. The copper content does not exceed 0.12 *apfu*. Minor contents of Cd (up to 0.05 *apfu*) and Sb (up to 0.07 *apfu*) were detected.

The dantopaite grain F4 in the sample ST 413 B3 (Fig. 3) is an anhedral grain with dimensions of *app.* 32 × 25 µm, partly in cavity, partly in arsenopyrite. This grain (points 10 - 15 in Table 5) is the Ag,Bi richest, i.e. has the lowest

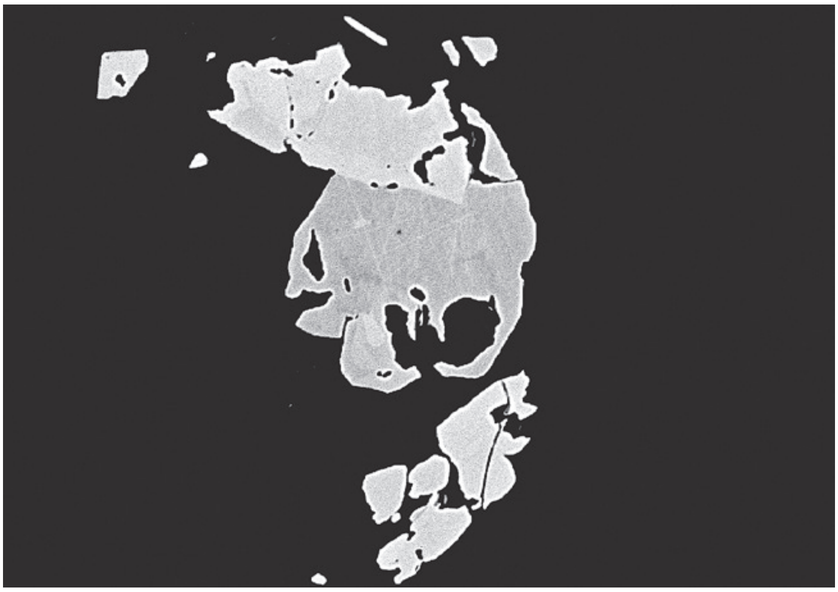

Fig 7 *Grains of cassiterite (top and bottom grains light grey, points 159, 160; middle grain darker grey, points 156, 157) in arsenopyrite (black) of sample ST 414 E2. Field of view 300 µm. BSE image of polished section ST 414 E2.*

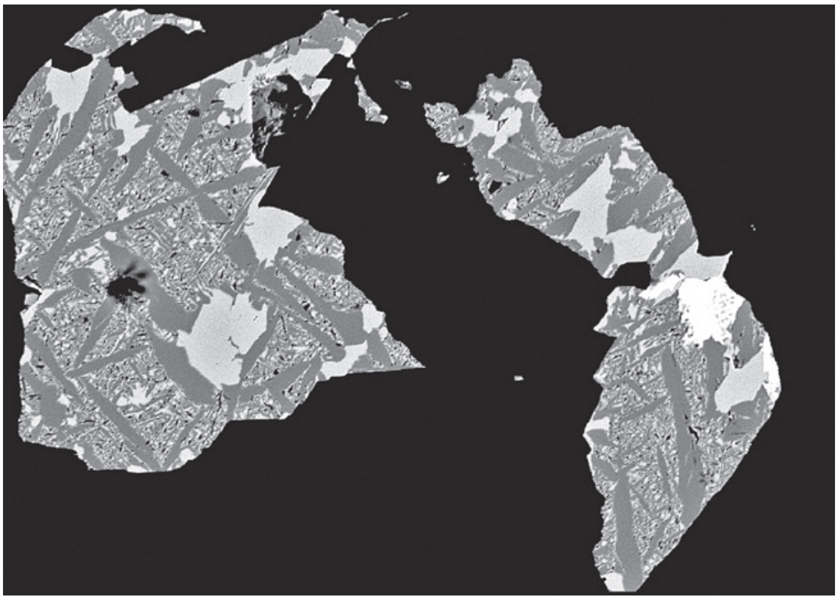

Fig 8 *Aggregates of Ag-Bi meralization with myrmekite-like structure in arsenopyrite (black); grains of Ag,Bi-rich galena (very light grey) with native bismuth (white) and matildite (dark grey). Field of view 350 µm. BSE image of sample ST 413 B3.*

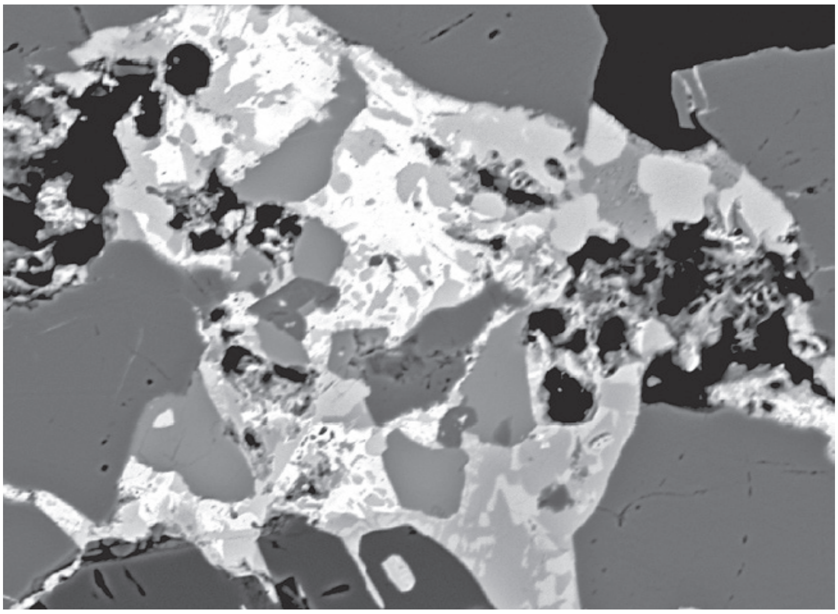

Fig 9 *An aggregate demonstrating complex replacement processes contains native bismuth (white, pt 55), Ag,Bi-rich galena (very light grey, pt 54), matildite (light grey, pt 53), acanthite (top right, pt 131, grey), kenoargentotetrahedrite--(Fe) (dark grey, pt 56), hosted by pyrrhotite at the bottom and arsenopyrite on the right. Field of view 200 µm. BSE image of sample ST 413 B3.*

content of Pb (0.56 - 0.64 *apfu*, i.e. 2.97 - 3.38 wt. %) among the four analysed grains. The average empirical formula is $Ag_{3.62}Cu_{0.25}(Pb_{0.59}Fe_{1.07}Cd_{0.03})_{\Sigma 1.69}(Bi_{12.02}Sb_{0.23})_{\Sigma 12.25}S_{22}$. Compared to other grains, this one shows the highest contents of Cu (0.23 - 0.29 *apfu*, i.e. 0.40 wt. %, mean of six analyses), at the same time it has also the highest levels of antimony (0.23 *apfu*, i.e. 0.72 wt. %, mean of six analyses), nearly three times higher than other three grains.

The iron content was a sort of a mystery as the grains are embedded in arsenopyrite and iron in the chemistry of dantopaite was reported only from one of the five localities (Jeleň et al. 2012). To establish whether the Fe content comes from neighbouring arsenopyrite the analyses were re-measured at 15 kV, at which voltage the iron content should decrease considerably as a result of smaller excitation volume if iron is not present in dantopaite. On the other hand, if the iron is indeed in dantopaite, the measured content should remain the same (or similar). The results are in Tables 2 to 5, points re-measured with lower voltage are marked R. The iron content indeed decreased, but only slightly, not enough to justify the explanation of Fe origin from arsenopyrite. No arsenic was detected at neither 25 or 15 kV. The re-measurement of the grain at lower voltage resulted in all cases to a small decrease of Fe and an increase of Bi and an even smaller increase in silver. Lead and copper contents were not affected and remained unchanged. The issue was discussed with Dan Topa (pers.comm.) and the general opinion was that the iron can be from dantopaite. Divalent metals such as Fe, Cd and Mn are known to substitute lead in sulfosalts (e.g. andorite series), although this phenomenon has so far not been observed in dantopaite with the exception of Hodruša, Slovakia (Jeleň et al. 2012), who found up to 1.31 wt. % Fe in dantopaite - a similar value as in Kutná Hora - and up to 3.26 wt. % in mummeite (pavonite homologue with N = 8). To unequivocally verify where the measured iron comes from would require single-crystal structure analysis which was not possible to carry out due to small size of the grains.

Table 7 *Chemical composition of cassiterite in arsenopyrite of sample ST 414 E2 (wt. %, apfu). Darker grain points 156, 157; lighter grain points 159, 160*

point	156	157	159	160
TiO_2	0.26	0.54	0.22	0.83
SnO_2	100.51	99.63	99.16	99.21
FeO	0.05	0.06	0.34	0.09
V_2O_3	0.10	0.07	0.00	0.16
Total	100.92	100.30	99.72	100.29
Ti	0.005	0.010	0.004	0.015
Sn	0.993	0.988	0.992	0.981
Fe	0.001	0.001	0.007	0.002
V	0.002	0.001	0.000	0.003
O	2.000	2.000	2.000	2.000

Iron contents in all four samples are positively correlated with lead contents, i.e. compositions with higher Pb showed higher iron levels. This supports the assumption that the iron is indeed an integral part of dantopaite chemistry and may substitute together with Pb at the Bi2 site, assumed by Makovicky et al. (2010) to concentrate lead.

The results show that three out of the four grains - those in Table 2, 4 and 5 - have a surplus of iron over lead.

Table 8 *Compositions of associated minerals in sample ST 413 B3 (Aca - acanthite, Bi - native bismuth, Gn - Bi,Ag--rich galena, Mtd - matildite, ttr - kenoargentotetrahedrite-(Fe), Sp - sphalerite, Stn - In-rich stannite)*

point	131	132	50	51	52	53	54	55	56	57	58	59	60
mineral	Aca	Aca	Bi	Gn	Mtd	Mtd	Gn	Bi	Ttr	Sp	Sp	Stn	Stn
Ag	87.42	87.84	0.00	1.90	28.49	28.30	1.85	0.00	33.90	0.00	0.00	0.08	0.09
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	13.14	0.34	0.22	29.16	28.86
Pb	0.15	0.00	0.00	80.69	0.16	0.00	81.36	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.18	0.21	0.00	0.31	0.03	0.36	0.47	0.00	5.36	10.16	10.46	12.48	12.71
Cd	0.10	0.09	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.56	0.57	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.60	0.82	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.52	54.10	53.31	1.62	2.76
In	0.00	0.00	0.07	0.06	0.00	0.00	0.05	0.05	0.00	0.15	0.12	0.13	0.31
Sn	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00	27.86	26.97
Sb	0.00	0.00	0.12	0.00	0.46	0.27	0.00	0.09	25.95	0.00	0.00	0.00	0.00
Bi	0.00	0.00	99.50	3.71	52.36	52.20	3.62	98.73	0.00	0.00	0.00	0.00	0.00
S	10.35	10.51	0.00	13.89	16.99	17.00	13.66	0.00	19.97	33.40	33.81	29.34	29.27
total	98.20	98.65	99.69	100.69	98.49	98.13	101.03	98.94	98.84	99.31	99.31	100.67	100.97
Ag	2.13	2.12	0.04	0.04	1.01	1.00	0.04	0.00	6.23	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	4.10	0.01	0.00	1.97	1.94
Pb	0.00	0.00	0.00	0.90	0.00	0.00	0.91	0.00	0.01	0.00	0.00	0.00	0.00
Fe	0.01	0.01	0.00	0.01	0.00	0.02	0.02	0.00	1.90	0.18	0.18	0.96	0.97
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.16	0.80	0.78	0.11	0.18
In	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.01
Sb	0.00	0.00	0.21	0.00	0.01	0.01	0.00	0.16	4.23	0.00	0.00	0.00	0.00
Bi	0.00	0.00	99.55	0.04	0.95	0.95	0.04	99.32	0.00	0.00	0.00	0.00	0.00
S	0.85	0.85	0.00	1.00	2.02	2.02	0.99	0.00	12.35	1.00	1.01	3.94	3.91

Empirical formulas were calculated on the basis of n *apfu*; n = 3 for acanthite, n = 2 for galena, n = 4 for matildite, n = 29 for kenoargentotetrahedrite-(Fe), n = 2 for sphalerite, n = 8 for stannite.

Provided all the iron is indeed from dantopaite and that all divalent metals lead and iron are concentrated at the Bi2 site in the structure of dantopaite (Makovicky et al. 2010), it is not ruled out that according to the IMA rules we may deal with a new mineral species. However, this would have to be decided by single-crystal diffraction. Interestingly, only the grain in Table 3, which is the composition with highest Pb content, has the surplus of lead over iron.

Associated minerals

As mentioned above both samples are formed by massive sulfide ore with no macroscopic presence of silver minerals or galena or any minerals except for base metal sulfides, of which arsenopyrite is the most abundant and dominating, followed by pyrrhotite and chalcopyrite. However back-scattered electron photographs revealed a fairly varied group of associated minerals contained mostly in arsenopyrite.

In polished section ST 414 E2, the arsenopyrite of the massive ore shows a distinct chemical zoning in the BSE images (Fig. 4), caused by AsS_{-1} substitution: in the BSE, the brighter parts are richer in As than the darker ones. The determined range of this substitution (1.04 - 1.05 and 1.13 - 1.14 *apfu* S, respectively - Table 6) is comparable with that published by Kretschmar, Scott (1976) or Sharp et al. (1985). Stannite occurs as aggregates up to 100 µm in size (Fig. 4) with minor In contents (points 57 and 58 in Table 6). Arsenopyrite contains inclusions of Ag,Bi-rich galena of 400 × 100 µm in size (Fig. 5, bottom left part) which is being replaced by kenoargentotetrahedrite-(Fe). Figure 6 (a detail cut-out of the bottom left part of Fig. 5) shows an inclusion of native bismuth (point 75 in Table 6) of 120 × 100 µm in size which is replaced by Ag,Bi-rich galena (point 76 in Table 6). Both minerals are replaced by kenoargentotetrahedrite-(Fe) with 6.10 - 6.23 *apfu* Ag and 12.34 - 12.49 *apfu* S (points 72 - 74 in Table 6). The right top part of Figure 5 shows a grain of Ag,Bi-rich galena which is being replaced by stephanite. A surplus of silver and a deficit of sulfur may result from the microbe measurement (inclined to over-measure silver and under-measure sulfur at standard conditions). Interesting is also the find of subhedral grains of cassiterite, 200 × 100 µm in size, in arsenopyrite (Fig. 7). Cassiterite was found to be zonal in BSE images with the middle part of the grain displaying darker shades of grey than the rest of the aggregate, nonetheless this is not strikingly reflected in chemistry between dark and light cassiterite (Table 7), although both show certain variability in minor contents of Fe and Ti. In most cases, cassiterite in Kutná Hora ore district belongs to the oldest minerals of the deposit (Hoffman, Trdlička 1976), sometimes it can be syngenetic with the early sulfide stage. Novák et al. (1962) described the replacement of cassiterite by stannite. Cases of cassiterite replacing other minerals are also known.

In polished section ST 413 B3, aggregates of Ag-Bi mineralization up to 300 µm in size with myrmekite-like structure (Fig. 8) were observed. They contain native bismuth (point 50 in Table 8), matildite (point 52) and Ag,Bi-rich galena (point 51). Another complex replacement processes are demonstrated in Fig. 9. An aggregate of 200 × 200 µm in size in pyrrhotite (at the bottom) and arsenopyrite (on the right and top) consists of native bismuth (point 55 in Table 8) replaced by Ag,Bi-rich galena (point 54) and matildite (point 53) which are subsequently being replaced by kenoargentotetrahedrite-(Fe) with 6.23 *apfu* of Ag and 12.35 *apfu* S (point 56 in Table 8). The latest mineral in Fig. 9 is acanthite (top right) replacing Ag,Bi-rich galena. Its not ideal stoichiometry is probably caused by well-known instability of acanthite under EPMA measurement conditions. Chalcopyrite is also present in the massive sulfide ore. It contains large grains of Fe,Mn,Cd-rich sphalerite (Fig. 10), typical of Kutná Hora ore district, which is replaced by In-bearing stannite with up to 0.31 wt. % of indium (0.01 *apfu*) (Table 8). Interestingly, in one instance a grain of a REE mineral was found in arsenopyrite in the polished section of ST 413 B3 with 30.33 wt.% Ce_2O_3 (average of four analyses), 16.36 wt. % La_2O_3, 11.77 wt. % Nd_2O_3 and 16.44 wt. % P_2O_5.

Conclusions

The first occurrence of dantopaite in the Czech Republic and the first occurrence of any pavonite homologue from Kutná Hora ore district and the associated minerals are described. The four described dantopaite grains represent four different compositions with regard to the lead content as a result of a different Ag + Bi = 2 Pb substitution in each grain. A distinct feature of all compositions is the content of iron, previously described in this mineral at only one of the five known localities. In three out of four grains, iron exceeds lead. Associated minerals in arsenopyrite of the massive sulfide ore can be classified as: a) minerals of the early sulfide stage (sphalerite, stannite) and cassiterite; b) minerals of the second sulfide stage: kenoargentotetrahedrite-(Fe) and minerals of the Ag-Bi mineralization (native bismuth, matildite, Ag,Bi-bearing galena, dantopaite; c) minerals of the latest Ag-Sb period (acanthite, stephanite).

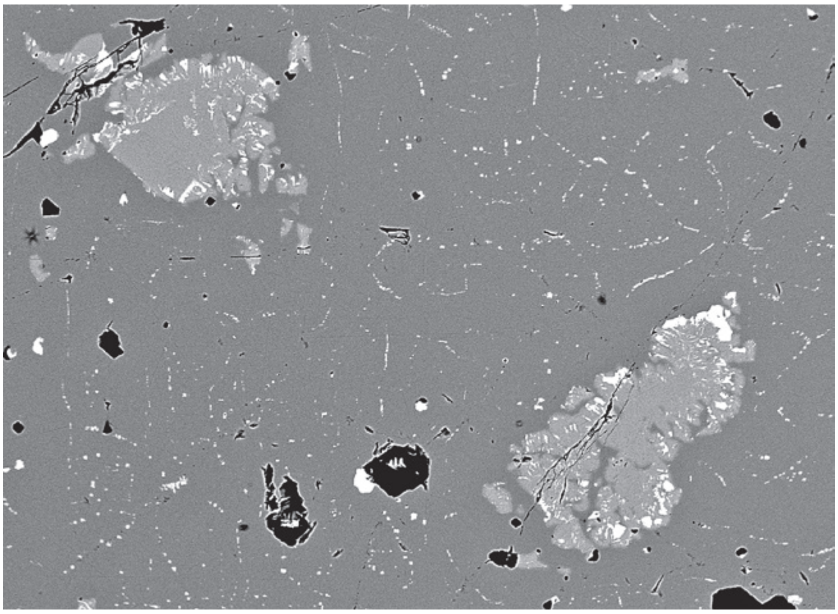

Fig 10 *Chalcopyrite (dark grey) with minute inclusions of stannite (white) and aggregates of Fe,Mn,Cd-rich sphalerite (light grey, points 57 and 58 in Table 7) which is partly replaced by indium-bearing stannite (white). Field of view 800 µm. BSE image of sample ST 413 B3.*

Acknowledgements

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