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Sb-enriched association of Ni arsenides and sulfarsenides from the Zemberg-Terézia vein system near Dobšiná (Western Carpathians, Slovak Republic)

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Abstract

An interesting association of Sb-enriched Ni arsenides and sulfarsenides was recently discovered in the carbonate-quartz (siderite type) hydrothermal vein in the Karol adit, at the Zemberg-Terézia vein system near Dobšiná, Slovak Republic. It is represented by nickeline and gersdorffite as main ore minerals accompanied by rammelsbergite, ullmannite, millerite, tetrahedrite-(Zn), chalcopyrite and bornite. The two distinct compositional types of nickeline are present, the Sb-poor (with up to 0.03 *apfu* of Sb) and Sb-rich variety (with up to 0.12 *apfu* of Sb). Gersdorffite is mostly replacing nickeline as rims or it forms aggregates, rims around or veinlets in tetrahedrite-(Zn). The three compositionally different types of gersdorffite are present: Sb-rich (with Sb reaching up to 0.31 *apfu*) and variable Ni/Co/Fe ratio, As-rich gersdorffite (with up to 1.32 *apfu* of As) also containing minor Co and Fe and the last one is Fe-rich gersdorffite (with up to 0.24 *apfu*) and nearly ideal As/S ratio. Rammelsbergite, ullmannite and millerite occur as abundant, microscopic inclusions in nickeline and gersdorffite. In tetrahedrite-(Zn), Zn (up to 1.52 *apfu*) is dominant over (Fe up to 0.82, Ni up to 0.12, Hg up to 0.04 and Pb up to 0.01 *apfu*) and Sb is considerably prevailing (2.96 - 4.01 *apfu*) over As (0.02 - 1.02 *apfu*). Both chalcopyrite and bornite were observed as inclusions in tetrahedrite-(Zn).

Key words: *nickeline, gersdorffite, rammelsbergite, ullmannite, arsenides, sulfarsenides, chemical composition, siderite veins, Dobšiná, Slovak Republic*

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Introduction

The hydrothermal carbonate (siderite, ankerite-dolomite series)-quartz veins around Dobšiná represent the most important accumulation of Ni arsenides and sulfarsenides in the Western Carpathians and in the past were significant producers of the high-grade Ni and Co ores in Europe. Despite other scattered occurrences of Ni sulfarsenides, especially gersdorffite at the hydrothermal siderite-quartz veins in the Spišsko-gemerské rudohorie Mts. (e.g. Rudňany - Bernard 1954; Hurný and Krištín 1978; Rožňava - Ulrich 1931, Varček 1959; Gelnica-Prakovce area - Bernard 1961, Háber 1976 or Úhorná - Peterec 1991) the veins around Dobšiná remain unique because Ni sulfarsenides are major ore minerals instead of generally much more common and prevailing chalcopyrite or tetrahedrite. Mineralogy of these veins was studied in detail using mostly ore-microscopy methods, especially in the 1950s and 1960s (Goll 1936, 1938; Paděra 1954, 1962; Halahyjová-Andrusovová 1957, 1959, 1964a, 1972). Chemical composition of sulfarsenides and arsenides from Dobšiná was subsequently studied by Husár (1982), Flassiková (1991), Chovan (1995), Chovan, Ozdín (2003), Števko et al. (2013) and Kyrc (2019). Relatively detailed study based mostly on older ore samples collected by Halahyjová-Andrusovová in 1950s-1960s was recently published by Keifer et al. (2017).

In this paper, we present new data on chemical composition of Ni arsenides, sulfarsenides and associated minerals from nickeline dominant, Sb-enriched association of ore minerals, which was recently discovered in Karol adit, at the Zemberg-Terézia vein system near Dobšiná.

Geological setting and occurrence

The Zemberg-Terézia vein system is located around 2.5 km NE of Dobšiná town, on the S and SW slopes of the Kruhová hill in the Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Eastern Slovakia. The most significant mining activity around Dobšiná is connected with the exploitation of nickel and cobalt ores particularly from this vein system. The Zemberg-Terézia vein system was extensively mined since 1780 until 1897. This area was later explored in detail in 1950s (Hladík, Kotras 1958) and also in late 1980s - early 1990s (Zlocha et al. 1986; Mesarčík et al. 1992), but only insignificant reserves of Ni-Co ores were discovered. New exploration for cobalt ores was recently conducted there by CE Metals Co. in 2017 and ceased in 2019. GPS coordinates of the Karol adit are: 48°50.387’ N and 20°22.988’ E.

The system of siderite-type hydrothermal carbonate-quartz veins with Ni-Fe-Co-Cu ore mineralization is hosted Early Paleozoic gneiss-amphibolite complex of the Klátov group belonging to the Gemeric unit (Rozložník 1959, 1965; Halahyjová-Andrusovová 1964b; Grecula et al. 1995; Mesarčík et al. 2001). The Zemberg-Terézia vein system is subdivided by N-S trending fault to western (Zemberg) and eastern (Terézia) segment. The Zemberg segment generally consists of three (Severná, Hlavná and Južná vein) and Terézia segment of two (Terézia I., Terézia II.) veins (Grecula et al. 1995; Mesarčík et al. 2001). The vertical extent of veins exceeds 1.5 km, generally with the SW-NE orientation and moderate to steep dip (40° to 70°) to the south or south-east. The veins are usually 0.7 to 1.5 m thick. Two different types of ore mineralization were distinguished at the veins in the Zemberg segment. Carbonate (siderite, ankerite-dolomite)-quartz vein filling with baryte and abundant chalcopyrite and tetrahedrite is typical for the upper parts of the veins, whereas Ni-Co-As minerals are prevailing ore minerals at the deeper parts of the veins (Halahyjová-Andrusovová 1959, 1964a; Grecula et al. 1995; Mesarčík et al. 2001). The dominant gangue minerals are carbonates, mainly Fe-dolomite-ankerite and siderite with quartz and minor tourmaline. Gersdorffite and arsenopyrite are the most frequent ore minerals, accompanied by minor pyrite, cobaltite, nickelskutterudite-skutterudite, löllingite, chalcopyrite, tetrahedrite, Bi sulphosalts and hematite (Halahyjová-Andrusovová 1959; Kiefer et al. 2017). Števko (in press) recently described also presence of abundant cinnabar in siderite-baryte vein filling of the topmost parts of the veins in the Zemberg segment. Hurai et al. (2002, 2015) connected origin of the siderite-type carbonate-quartz veins with sulphides in the Spišsko-gemerské rudohorie Mts. with the Alpine magmatic-metamorphic processes.

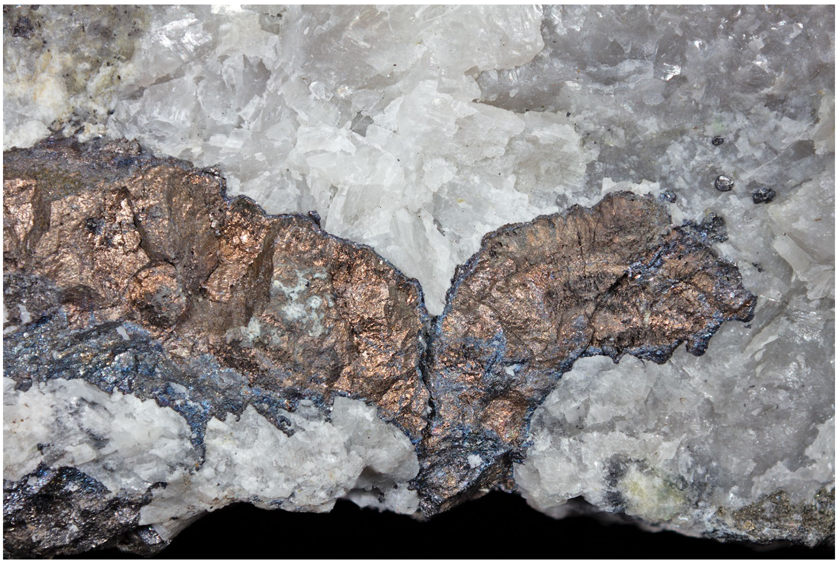
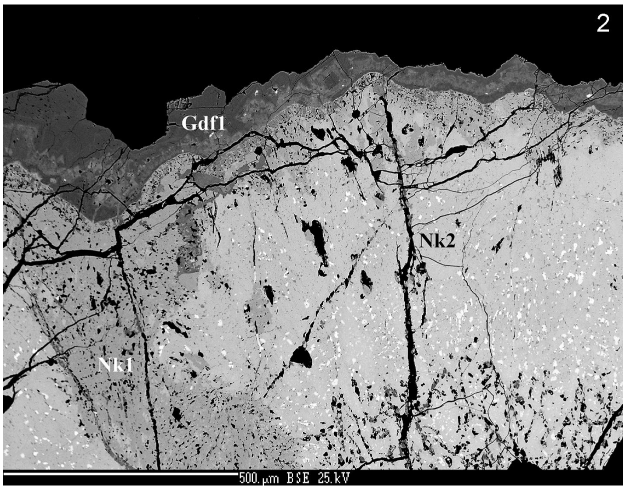
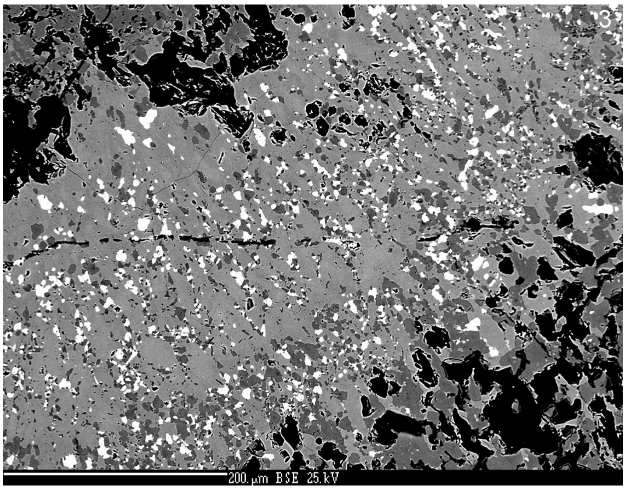


Fig. 1 *Copper red aggregates of nickeline with bluish-grey rim of gersdorffite embedded in white coarse-grained Fe-rich dolomite gangue. Photo by P. Škácha, field of view is 17 mm.*





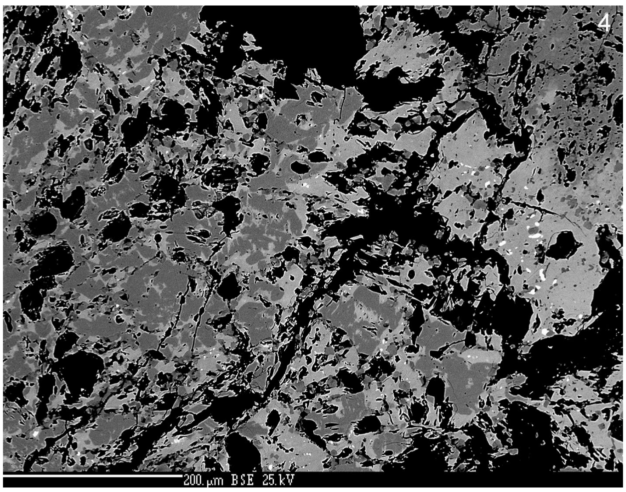


Fig. 2 *Two compositional types of nickeline (Nk1 is Sb -poor and Nk2 is Sb-rich variety) with abundant tiny inclusions of ullmannite (white) rimmed by zonal Sb-rich gersdorffite (Gdf1, type 1). BSE image by Z. Dolníček.*

Fig. 3 *Detail on aggregate of nickeline (light grey) with abundant inclusions of ullmannite (white) and rammelsbergite (dark grey). BSE image by Z. Dolníček.*

Fig. 4 *Detail on two compositional types of nickeline: Sb -poor (dark grey) and Sb-rich (light grey). Tiny white inclusions are ullmannite. BSE image by Z. Dolníček.*

Kiefer et al. (in press) recently confirmed Cretaceous age of the hydrothermal veins with Ni-Co mineralization in Dobšiná area using U/Pb dating of vein carbonates and Re/Os dating of gersdorffite.

Samples with arsenides were collected *in-situ* underground in the Karol adit (from the sublevel driven on the Južná vein above the Karol adit, which is accessible via inclined raise) from the lenticular hydrothermal carbonate (mainly Fe-dolomite) vein with minor quartz. This vein is up to 8 cm thick and it is hosted in hydrothermally altered gneiss with minor pyrite impregnations.

Analytical methods

The ore minerals, their relationships and textures were first studied in reflected light using a Nikon Eclipse ME600 polarizing microscope (National Museum, Prague, Czech Republic).

The chemical analyses of individual ore minerals were performed using a Cameca SX100 electron microprobe (National Museum, Prague, Czech Republic) operating in the wave-dispersive (WDS) mode (25 kV, 20 nA and 0.7 µm wide beam). The following standards and X-ray lines were used to minimize line overlaps: Ag (AgLα), apatite (CaKα, PKα), Au (AuMα), baryte (BaLα), Bi_2Se_3 (BiMβ), CdTe (CdLα), Co (CoKα), $CuFeS_2$ (CuKα, SKα), FeS_2 (FeKα), GaAs (GaLα), Ge (GeLα), HgTe (HgLα), InAs (InLα), Mn (MnKα), NaCl (ClKα), NiAs (AsLβ), Ni (NiKα), PbS (PbMα), PbSe (SeLβ), PbTe (TeLα), sanidine (KKα), Sb_2S_3 (SbLα), Sn (SnLα) and ZnS (ZnKα). Contents of the above-listed elements, which are not included in the ta-

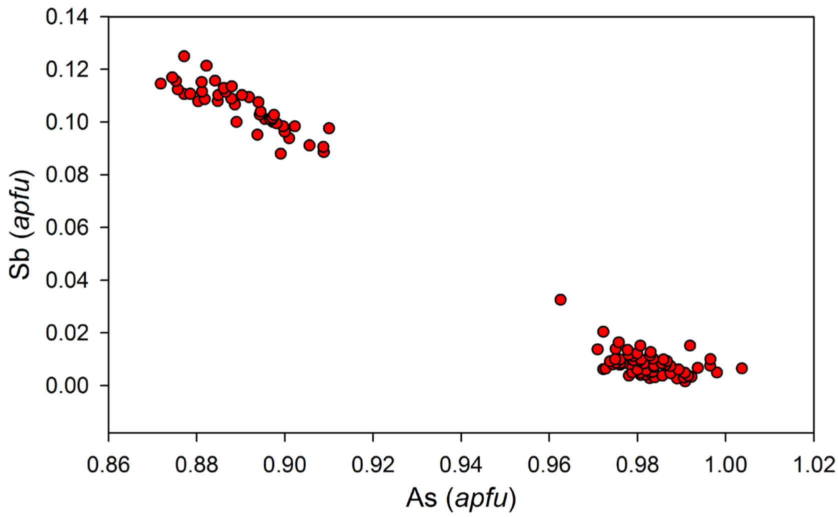


Fig. 5 *Variation of Sb and As (apfu) in nickeline from Dobšiná. The two types of compositions (Sb-poor and Sb-rich) are clearly visible.*

Table 1 *Representative WDS analyses of Sb-poor nickeline from Dobšiná (wt.%)*

	mean	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ni	44.52	44.18	44.97	44.25	44.24	44.84	44.77	43.77	44.35	44.67	44.72	43.54	44.59	43.98	43.74
Co	0.01	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.07	0.00
Sb	0.77	0.14	0.26	0.30	0.34	0.38	0.55	0.69	0.73	0.79	0.85	0.91	1.08	1.85	2.94
As	55.47	55.74	55.73	55.78	55.71	55.71	55.46	56.05	55.63	55.25	55.37	55.90	55.65	54.38	53.47
S	0.07	0.13	0.06	0.00	0.00	0.09	0.11	0.07	0.05	0.20	0.00	0.07	0.17	0.06	0.00
total	100.84	100.19	101.02	100.33	100.29	101.10	100.89	100.58	100.76	100.91	100.94	100.42	101.65	100.34	100.15
Ni	1.006	1.002	1.012	1.004	1.005	1.009	1.010	0.993	1.004	1.007	1.010	0.991	1.000	1.003	1.005
Co	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.001	0.000
Sb	0.008	0.002	0.003	0.003	0.004	0.004	0.006	0.008	0.008	0.009	0.009	0.010	0.012	0.020	0.033
As	0.982	0.991	0.983	0.992	0.991	0.982	0.980	0.996	0.986	0.976	0.980	0.997	0.978	0.972	0.963
S	0.003	0.005	0.002	0.000	0.000	0.004	0.005	0.003	0.002	0.008	0.000	0.003	0.007	0.003	0.000

mean - average of 61 analyses; 1-14 representative analyses; calculated empirical formulae are based on sum of 2 *apfu*

Table 2 *Representative WDS analyses of Sb-rich nickeline from Dobšiná (wt.%)*

	mean	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ni	42.75	42.97	42.73	42.73	42.63	42.62	42.61	42.63	42.81	42.28	42.45	42.59	42.31	42.15	42.20
Co	0.03	0.28	0.06	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb	9.33	7.87	8.03	8.32	8.68	8.82	8.91	9.06	9.52	9.75	9.95	10.13	10.15	10.64	10.96
As	48.45	49.50	49.58	49.14	48.84	48.67	48.53	48.51	47.99	47.74	48.08	47.71	47.73	47.62	47.34
S	0.02	0.26	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00
total	100.58	100.88	100.40	100.37	100.15	100.11	100.05	100.20	100.32	99.77	100.54	100.43	100.19	100.41	100.50
Ni	1.003	0.996	0.999	1.000	1.002	1.003	1.003	1.003	1.007	1.002	0.998	1.004	1.000	0.996	0.998
Co	0.001	0.006	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sb	0.105	0.088	0.091	0.094	0.098	0.100	0.101	0.103	0.108	0.111	0.113	0.115	0.116	0.121	0.125
As	0.890	0.899	0.909	0.901	0.900	0.897	0.895	0.894	0.885	0.887	0.886	0.881	0.884	0.882	0.877
S	0.001	0.011	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000

mean - average of 43 analyses; 1-14 representative analyses; calculated empirical formulae are based on sum of 2 *apfu*

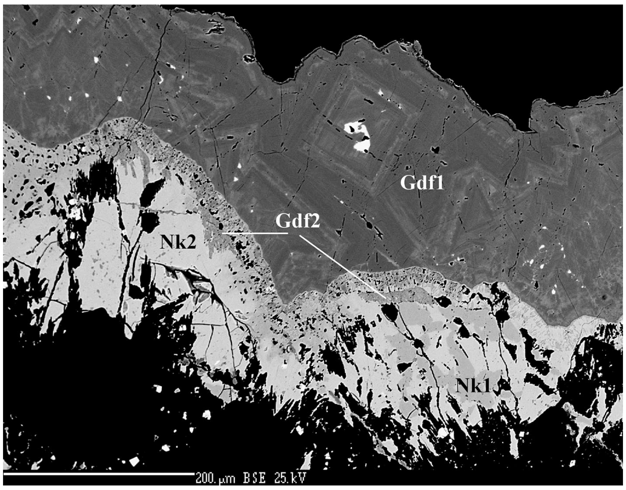


Fig. 6 *The rim of Sb-rich gersdorffite (Gdf1, type 1) with oscillatory zoning is overgrowing older aggregate of zonal Sb-poor (Nk1) and Sb-rich (Nk2) nickeline. As-rich gersdorffite (Gdf2, type 2) forms thin rim and irregular aggregates developed around the boundary of Sb-rich gersdorffite and nickeline. White inclusions are ullmannite. BSE image by Z. Dolníček.*

bles, were analysed quantitatively, but their contents were below the detection limit (ca. 0.03 - 0.05 wt. % for individual elements). Raw intensities were converted to the concentrations of elements using automatic "PAP" matrix-correction software (Pouchou, Pichoir 1985).

Results

Nickeline is the dominant ore mineral in the studied association. It forms irregular, botryoidal to spherical aggregates up to 2 cm in size or elongated veinlets up to 3 cm long and 1 cm thick enclosed in Fe-rich dolomite (Fig. 1). It has typical copper red colour and metallic lustre. Nickeline is clearly the oldest ore mineral, which is often rimmed or replaced by later gersdorffite (Fig. 2) and it also contain abundant inclusions of younger ullmannite or rammelsbergite (Fig. 3).

The two distinct compositional types of nickeline (darker vs. lighter in BSE, Fig. 2, 4) were distinguished. They differ especially by the Sb/As ratio (Fig. 5). The first type is represented by Sb-poor nickeline (Tab. 1, Fig. 5), which contain up to 0.03 *apfu* of Sb and minor amounts of S (up to 0.01 *apfu*) and locally also Co (up to 0.003 *apfu*), with a mean composition (calculated from 61 analyses) of $Ni_{1.01}(As_{0.98}Sb_{0.01})_{\Sigma 0.99}$. The second type shows increased

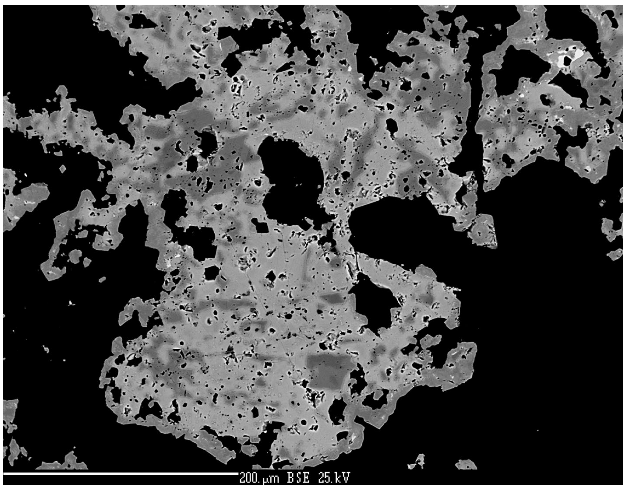


Fig. 7 *Aggregates of gersdorffite (type 3, dark grey) intergrown with tetrahedrite-(Zn) (light grey). BSE image by Z. Dolníček.*

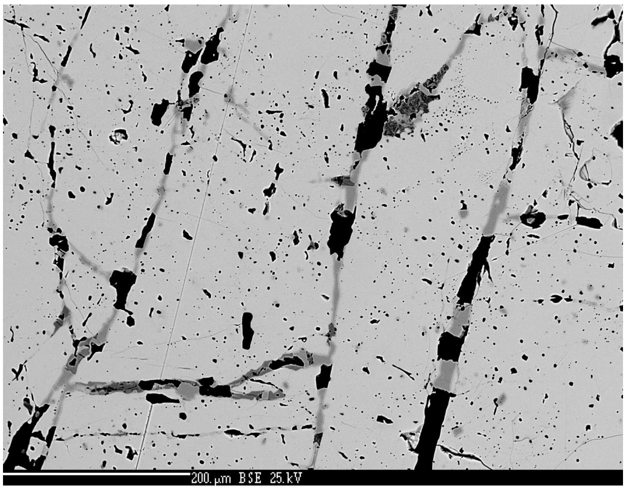


Fig. 9 *Thin veinlets of gersdorffite (type 3, dark grey) filling the fractures in tetrahedrite-(Zn) (light grey). BSE image by Z. Dolníček.*

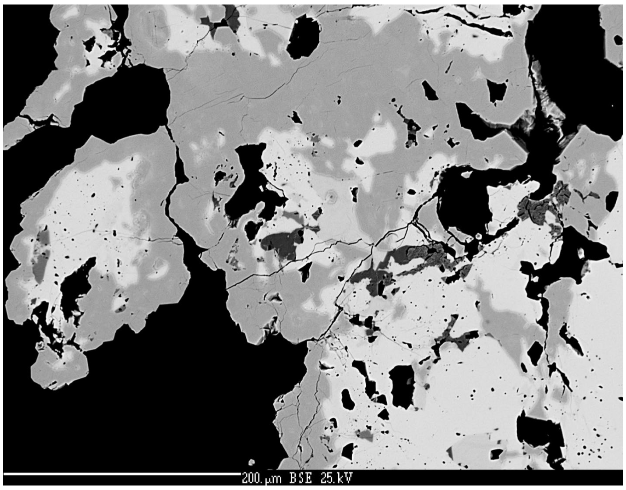


Fig. 8 *Rims of gersdorffite (type 3, light grey) around aggregates of tetrahedrite-(Zn) (white) with inclusions of chalcopyrite (dark grey). BSE image by Z. Dolníček.*

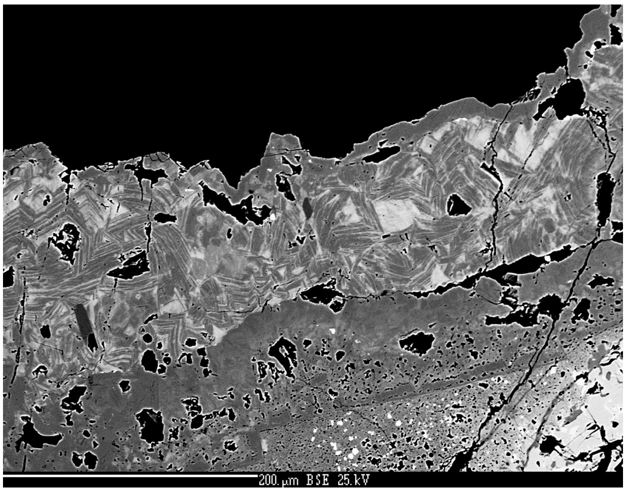


Fig. 10 *Detail on strong irregular to oscillatory zoning of Sb-rich gersdorffite (type 1). BSE image by Z. Dolníček.*

contents of Sb (between 0.09 to 0.12 *apfu*; Tab. 2, Fig. 5). The amount of Co and S is low (up to 0.01 *apfu*). The mean composition of Sb-rich nickeline (calculated from 43 analyses) is $Ni_{1.00}(As_{0.89}Sb_{0.11})_{\Sigma 1.00}$.

Gersdorffite occurs mostly as up to 200 μm thick polycrystalline rims, which are replacing aggregates of older nickeline (Fig. 6) and aggregates intergrown with tetrahedrite-(Zn) (Fig. 7) or rims around it (Fig. 8). Thin veinlets of gersdorffite filling the fractures in tetrahedrite-(Zn) were also observed (Fig. 9, 15).

Based on the study of chemical composition (176 analyses of gersdorffite were performed in total), the following three types of gersdorffite were distinguished: the first type (Tab. 3) is represented by rims around aggregates of nickeline, which show strong irregular to oscillatory zoning in BSE (Fig. 6, 10) and significant enrichment in Sb (up to 0.31 *apfu*) is characteristic (Fig. 11). The content of As+Sb and S in this type of gersdorffite is very close to the ideal ratio of 1:1, with the obvious negative correlation between As and S (Fig. 12), caused by AsS_{-1} isomorphism. Besides the dominant amounts of Ni (0.46 to 1.01 *apfu*), both Co (up to 0.48 *apfu*) and Fe (up to 0.32 *apfu*) are other major elements present in the Me site. The second, rare type of gersdorffite occurs as irregular aggregates replacing nickeline at the boundaries with the rims of Sb-rich gersdorffite (Fig. 6). This As-rich gersdorffite (Tab. 4) shows strong AsS_{-1} substitution (Fig. 12), with contents of S reaching only 0.62 - 0.71 *apfu*, but

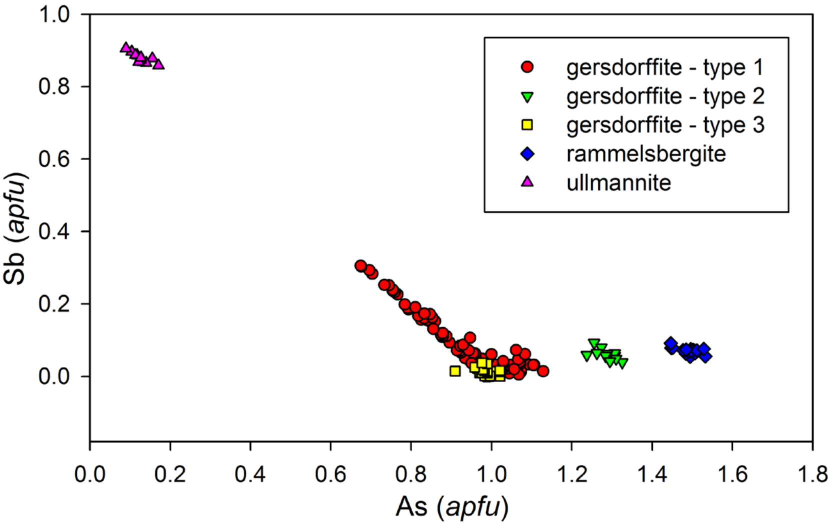


Fig. 11 *As vs. Sb (apfu) plot for gersdorffite, rammelsbergite and ullmannite from Dobšiná.*

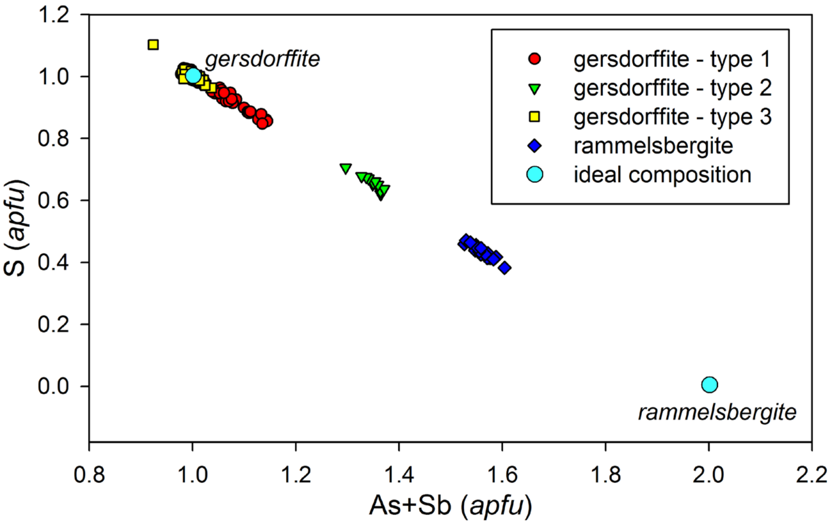


Fig. 12 *Variations of S vs. As+Sb (apfu) in various types of gersdorffite and rammelsbergite from Dobšiná.*

Table 3 *Representative WDS analyses of Sb-enriched gersdorffite (type 1) (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Fe	10.53	4.89	10.97	6.81	1.29	3.97	2.69	1.64	5.94	1.43	0.30	0.32	0.00	0.10
Pb	0.10	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00
Ni	20.02	30.62	20.02	25.76	15.94	31.24	26.39	33.05	27.36	33.48	33.16	34.25	33.44	33.21
Co	4.78	0.44	4.33	2.63	18.14	0.08	5.75	0.00	1.06	0.00	0.60	0.07	0.00	0.00
Sb	0.00	0.00	0.20	0.35	0.38	0.97	1.43	2.02	2.21	2.68	4.34	9.33	20.77	20.81
As	45.05	45.22	45.66	45.04	47.41	44.49	46.66	43.74	47.97	42.84	43.76	37.53	28.50	28.30
S	19.46	19.92	19.25	19.85	18.00	19.53	17.52	19.73	15.76	19.74	17.75	18.91	18.23	18.10
total	99.94	101.09	100.53	100.44	101.16	100.28	100.44	100.18	100.47	100.17	99.91	100.41	100.94	100.52
Fe	0.312	0.143	0.324	0.200	0.039	0.117	0.082	0.049	0.183	0.043	0.009	0.010	0.000	0.003
Pb	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Ni	0.564	0.850	0.563	0.721	0.458	0.879	0.762	0.934	0.804	0.948	0.967	0.996	1.012	1.010
Co	0.124	0.011	0.112	0.068	0.482	0.002	0.153	0.000	0.029	0.000	0.016	0.002	0.000	0.000
Σ	1.001	1.004	1.000	0.990	0.979	0.999	0.997	0.983	1.017	0.990	0.992	1.007	1.012	1.013
Sb	0.000	0.000	0.003	0.005	0.005	0.013	0.020	0.028	0.031	0.037	0.061	0.131	0.303	0.305
As	0.995	0.984	1.006	0.988	1.068	0.981	1.056	0.969	1.104	0.950	1.000	0.855	0.676	0.674
S	1.004	1.012	0.991	1.018	0.948	1.007	0.927	1.021	0.848	1.023	0.947	1.007	1.010	1.008
Σ	1.999	1.996	2.000	2.010	2.021	2.001	2.003	2.017	1.983	2.010	2.008	1.993	1.988	1.987

an. No. 5 is cobaltite; calculated empirical formulae are based on sum of 3 *apfu* in contrary As is reaching between 1.23 to 1.32 *apfu*, accompanied also by minor amounts of Sb (up to 0.09 *apfu*, Fig. 11). The major contents of Ni (0.77 - 0.96 *apfu*, Fig. 13) are accompanied by only minor contents of Co (up to 0.13 *apfu*) and Fe (up to 0.06 *apfu*). The third compositional type is represented by relatively homogenous aggregates or rims (Fig. 7, 8) directly associated with tetrahedrite-(Zn). In the Me site of this type of gersdorffite Ni is often accompanied by Fe (up to 0.24 *apfu*) and Co (up to 0.08 *apfu*) as well as by the minor amounts of Cu (up to 0.07 *apfu*) and Zn (up to 0.01 *apfu*). The contents of Sb (Tab. 5) are surprisingly low (reaching only up to 0.03 *apfu*) and the content of S (0.96 - 1.10 *apfu*) is close to the ideal value.

Rammelsbergite is frequent a mineral and forms anhedral to subhedral grains up to 100 μm in size enclosed in aggregates of nickeline (Fig. 3) or in gersdorffite rims (Fig. 14). The tentative identification of rammelsbergite is based on optical properties in reflected light, especially strong anisotropy.

Representative WDS analyses of rammelsbergite from Dobšiná are shown in Table 6. Besides the dominant contents of Ni (0.91 - 0.95 *apfu*), minor amounts of Co (up to 0.08 *apfu*) and also Fe (up to 0.04 *apfu*) were detected in Me site (Fig. 13). There are also relatively strong variations in As/S and Sb contents in studied rammelsbergite (Fig. 11, 12), with S content reaching up

Table 4 *Chemical composition of As-rich gersdorffite (type 2) (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11
Fe	1.00	1.23	1.26	1.60	1.22	1.21	1.35	1.50	1.76	1.28	1.38
Pb	0.00	0.42	0.29	0.18	0.29	0.22	0.23	0.58	0.12	0.42	0.21
Ni	30.94	26.02	25.69	25.50	25.72	26.33	26.42	25.48	24.86	25.98	26.18
Co	0.86	4.83	4.88	4.74	4.60	4.52	3.83	4.50	5.36	4.75	5.00
Sb	2.63	3.78	4.25	3.26	6.10	4.14	5.33	3.81	2.81	4.30	3.99
As	54.63	53.10	53.15	53.72	50.63	52.69	51.93	52.49	53.39	51.61	51.18
S	10.94	10.94	11.10	11.43	11.26	11.50	11.56	11.76	11.93	11.88	12.51
total	101.00	100.32	100.62	100.43	99.82	100.61	100.65	100.12	100.23	100.22	100.45
Fe	0.033	0.041	0.042	0.052	0.041	0.040	0.044	0.049	0.057	0.042	0.045
Pb	0.000	0.004	0.003	0.002	0.003	0.002	0.002	0.005	0.001	0.004	0.002
Ni	0.958	0.817	0.806	0.794	0.814	0.821	0.827	0.795	0.769	0.811	0.808
Co	0.025	0.140	0.141	0.136	0.134	0.130	0.111	0.130	0.153	0.137	0.143
Σ	1.015	1.002	0.992	0.984	0.992	0.993	0.984	0.979	0.981	0.994	0.997
Sb	0.039	0.057	0.064	0.049	0.093	0.062	0.080	0.057	0.042	0.065	0.059
As	1.325	1.307	1.307	1.310	1.256	1.288	1.273	1.283	1.295	1.262	1.237
S	0.620	0.629	0.638	0.651	0.652	0.657	0.662	0.672	0.676	0.679	0.707
Σ	1.985	1.993	2.008	2.010	2.001	2.007	2.016	2.013	2.013	2.006	2.003

calculated empirical formulae are based on sum of 3 *apfu*

Table 5 *Representative WDS analyses of gersdorffite (type 3) associated with tetrahedrite-(Zn) (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Fe	1.55	4.95	0.06	0.10	0.09	0.22	8.64	0.00	0.39	0.10	0.00	0.00	0.00	0.12
Pb	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00
Ni	32.50	28.88	34.63	34.56	34.54	33.23	25.32	34.58	32.02	33.40	34.62	33.50	35.04	34.28
Co	0.10	0.28	0.09	0.09	0.00	1.73	0.15	0.00	2.91	0.07	0.00	0.07	0.06	0.22
Zn	0.14	0.11	0.12	0.09	0.10	0.00	0.12	0.12	0.00	0.30	0.14	0.12	0.00	0.08
Cu	0.75	0.73	0.88	1.04	0.69	0.22	1.03	0.75	0.21	2.05	1.03	2.76	0.25	0.55
Sb	0.00	0.06	0.66	0.68	0.92	0.96	1.09	1.07	1.16	1.18	1.38	1.84	2.54	2.71
As	46.12	45.32	44.91	44.26	44.93	45.99	42.47	44.76	46.01	44.74	44.41	43.25	44.49	43.92
S	19.11	19.80	19.38	19.54	19.45	18.54	22.05	19.28	18.58	19.47	19.40	19.18	18.69	19.01
total	100.27	100.13	100.73	100.36	100.84	100.89	100.87	100.56	101.28	101.31	100.98	100.72	101.18	100.89
Fe	0.046	0.146	0.002	0.003	0.003	0.007	0.248	0.000	0.012	0.003	0.000	0.000	0.000	0.004
Pb	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Ni	0.918	0.810	0.974	0.973	0.971	0.943	0.692	0.976	0.907	0.936	0.974	0.947	0.995	0.973
Co	0.003	0.007	0.002	0.002	0.000	0.045	0.004	0.000	0.076	0.002	0.000	0.002	0.002	0.006
Zn	0.004	0.003	0.003	0.002	0.003	0.000	0.003	0.003	0.000	0.008	0.004	0.003	0.000	0.002
Cu	0.020	0.019	0.023	0.027	0.018	0.006	0.026	0.020	0.005	0.053	0.027	0.072	0.007	0.014
Σ	0.944	0.839	1.002	1.004	0.993	0.994	0.725	0.999	0.988	0.999	1.004	1.024	1.004	0.995
Sb	0.000	0.001	0.009	0.009	0.012	0.013	0.014	0.015	0.016	0.016	0.019	0.025	0.035	0.037
As	1.021	0.997	0.990	0.976	0.990	1.023	0.909	0.990	1.021	0.983	0.979	0.958	0.990	0.977
S	0.989	1.017	0.998	1.007	1.002	0.963	1.103	0.997	0.963	0.999	0.999	0.993	0.972	0.988
Σ	2.010	2.015	1.996	1.993	2.004	1.999	2.027	2.001	2.000	1.998	1.996	1.976	1.996	2.001

calculated empirical formulae are based on sum of 3 *apfu*

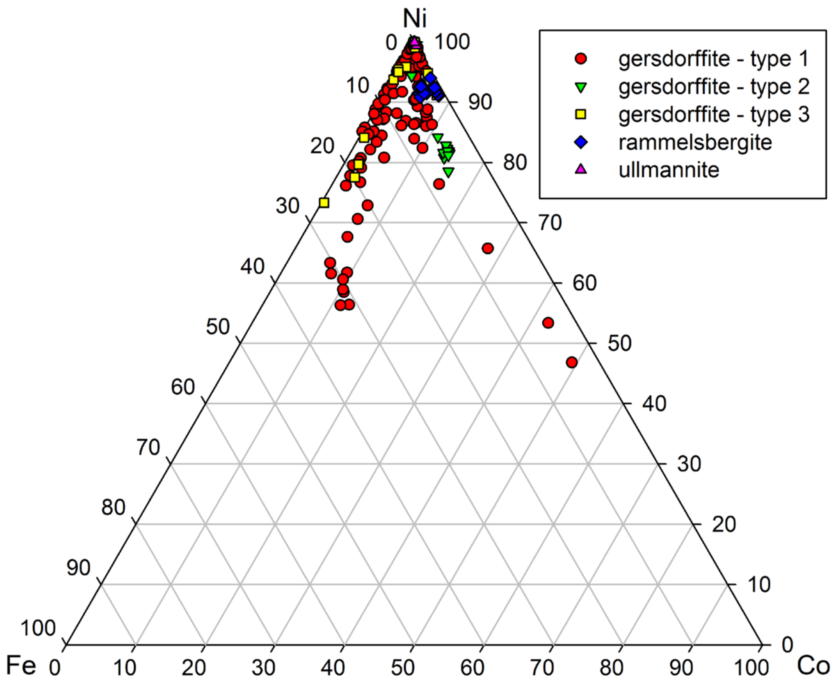


Fig. 13 *Ternary Fe-Co-Ni (apfu) plot for gersdorffite, rammelsbergite and ullmannite from Dobšiná.*

Table 6 *Representative WDS analyses of rammelsbergite from Dobšiná (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Fe	1.05	0.90	0.28	0.84	0.31	0.26	0.33	0.26	1.08	0.75	0.20	0.74	0.84	0.80
Ni	27.99	28.01	28.59	28.08	28.58	28.40	28.48	28.44	27.84	28.18	28.97	28.44	28.03	28.22
Co	1.69	1.52	2.71	1.66	2.63	2.45	2.41	2.24	1.81	1.52	1.77	2.03	1.88	1.54
Sb	3.49	3.51	4.07	4.10	4.33	4.44	4.59	4.57	4.61	4.69	4.79	5.00	5.01	5.81
As	58.74	59.67	58.61	58.76	58.73	58.76	58.26	59.02	57.78	57.84	59.34	56.64	56.79	56.42
S	7.66	6.95	7.42	7.17	7.18	7.17	7.32	6.87	7.54	7.44	6.36	7.69	7.89	7.75
total	100.62	100.56	101.68	100.61	101.76	101.48	101.39	101.40	100.66	100.42	101.43	100.54	100.44	100.54
Fe	0.036	0.031	0.010	0.029	0.011	0.009	0.011	0.009	0.037	0.026	0.007	0.025	0.029	0.028
Ni	0.909	0.918	0.924	0.919	0.926	0.924	0.925	0.929	0.908	0.923	0.952	0.928	0.914	0.923
Co	0.051	0.046	0.081	0.050	0.079	0.074	0.072	0.068	0.055	0.046	0.054	0.061	0.057	0.047
Σ	0.995	0.995	1.014	0.998	1.015	1.006	1.009	1.006	1.000	0.995	1.013	1.014	0.999	0.997
Sb	0.055	0.055	0.063	0.065	0.068	0.070	0.072	0.072	0.073	0.074	0.076	0.079	0.079	0.092
As	1.495	1.532	1.484	1.507	1.491	1.497	1.483	1.511	1.477	1.485	1.528	1.448	1.451	1.447
S	0.455	0.417	0.439	0.430	0.426	0.427	0.436	0.411	0.450	0.446	0.383	0.459	0.471	0.464
Σ	2.005	2.005	1.986	2.002	1.985	1.994	1.991	1.994	2.000	2.005	1.987	1.986	2.001	2.003

calculated empirical formulae are based on sum of 3 *apfu*

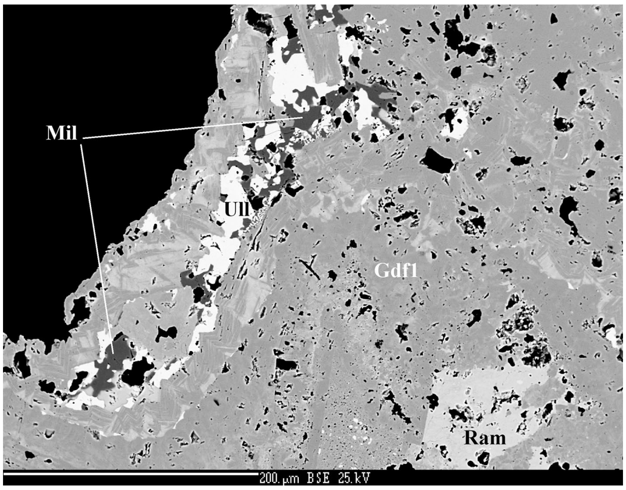


Fig. 14 *Polycrystalline rim of zonal Sb-rich gersdorffite (Gdf1, type 1) with subhedral grain of rammelsbergite (Ram) and inclusions of ullmannite (Ull) and millerite (Mil). BSE image by Z. Dolníček.*

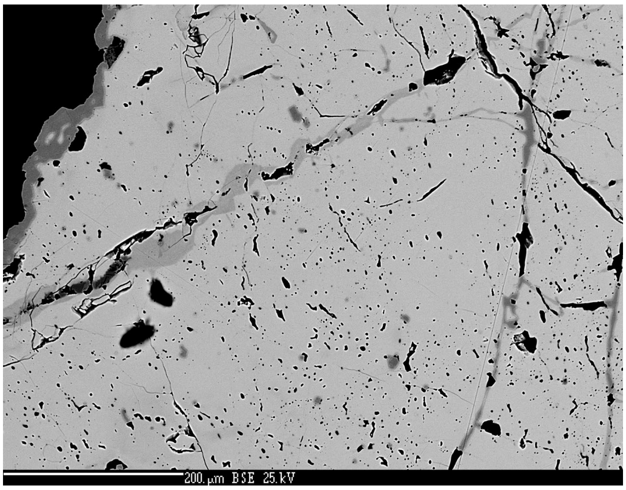


Fig. 15 *Veinlet of slightly As-enriched tetrahedrite-(Zn) (medium grey) in tetrahedrite-(Zn) (light grey). Thin dark grey veinlets and rim are gersdorffite (type 3). BSE image by Z. Dolníček.*

Table 7 *Chemical composition of ullmannite from Dobšiná (wt.%)*

	mean	1	2	3	4	5	6	7	8	9	10	11	12
Ni	28.33	27.92	28.22	28.41	28.26	28.29	28.11	28.28	28.21	28.11	28.96	28.64	28.59
Co	0.03	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00
Sn	0.14	0.10	0.17	0.09	0.13	0.12	0.12	0.14	0.14	0.16	0.14	0.15	0.16
Sb	51.80	51.21	51.03	51.23	51.43	51.99	52.24	52.28	52.60	50.35	51.46	52.47	53.32
As	4.58	5.58	4.76	5.10	4.55	4.64	4.25	4.30	3.76	6.16	4.44	4.13	3.25
S	15.42	14.91	15.54	15.54	15.53	15.55	15.58	15.55	15.45	14.96	15.53	15.47	15.46
total	100.29	99.83	99.72	100.37	99.90	100.59	100.30	100.55	100.16	99.93	100.53	100.86	100.78
Ni	0.997	0.992	0.995	0.996	0.996	0.992	0.990	0.993	0.997	0.994	1.013	1.004	1.006
Co	0.001	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.000
Sn	0.002	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.003	0.003
Σ	1.000	0.997	0.998	0.997	0.998	0.994	0.992	0.996	1.000	1.003	1.015	1.007	1.009
Sb	0.879	0.877	0.868	0.866	0.874	0.879	0.887	0.886	0.896	0.858	0.868	0.887	0.905
As	0.126	0.155	0.131	0.140	0.126	0.128	0.117	0.118	0.104	0.171	0.122	0.113	0.090
Σ	1.006	1.033	0.999	1.006	1.000	1.007	1.004	1.004	1.001	1.029	0.990	1.000	0.995
S	0.994	0.970	1.003	0.997	1.002	0.999	1.004	1.000	1.000	0.968	0.995	0.993	0.996

mean - average of 12 analyses; calculated empirical formulae are based on sum of 3 *apfu*

Table 8 *Chemical composition of millerite from Dobšiná (wt.%)*

	mean	1	2	3	4	5	6	7
Fe	0.19	0.19	0.25	0.20	0.13	0.09	0.31	0.17
Pb	0.11	0.11	0.15	0.10	0.06	0.10	0.17	0.05
Ni	63.42	63.60	63.60	63.55	63.64	62.81	63.24	63.50
Co	0.17	0.18	0.19	0.16	0.18	0.16	0.17	0.17
Cu	0.06	0.09	0.03	0.11	0.16	0.00	0.06	0.00
Sb	0.11	0.07	0.07	0.08	0.10	0.12	0.15	0.17
Te	0.09	0.07	0.11	0.06	0.09	0.06	0.12	0.12
S	35.60	35.83	35.45	35.59	35.54	35.28	35.81	35.68
total	99.75	100.14	99.85	99.85	99.90	98.62	100.03	99.86
Fe	0.003	0.003	0.004	0.003	0.002	0.001	0.005	0.003
Pb	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000
Ni	0.982	0.980	0.985	0.983	0.985	0.983	0.977	0.982
Co	0.002	0.003	0.003	0.002	0.003	0.002	0.002	0.002
Cu	0.001	0.001	0.000	0.002	0.002	0.000	0.001	0.000
Σ	0.989	0.988	0.993	0.991	0.992	0.987	0.986	0.987
Sb	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Te	0.001	0.000	0.001	0.000	0.001	0.000	0.001	0.001
S	1.009	1.011	1.006	1.008	1.007	1.011	1.012	1.010
Σ	1.011	1.012	1.007	1.009	1.008	1.013	1.014	1.013

mean - average of 7 analyses; calculated empirical formulae are based on sum of 2 *apfu*

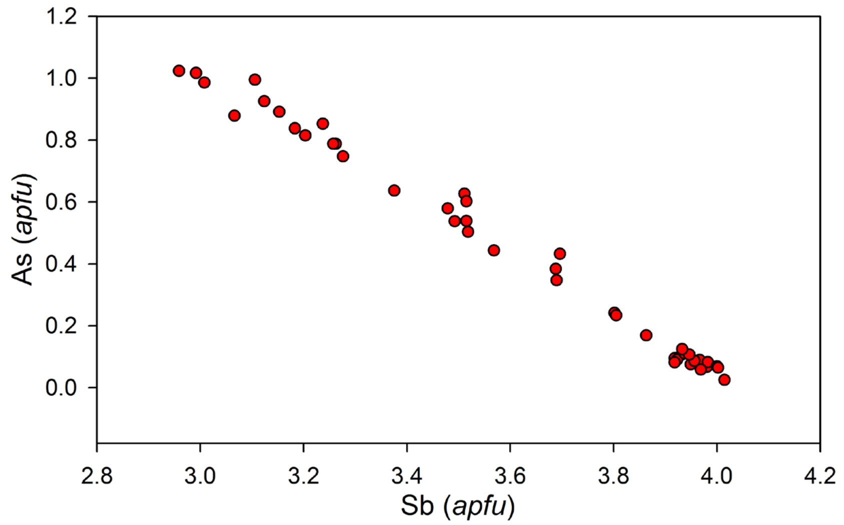


Fig. 16 *Sb vs. As (apfu) plot for tetrahedrite-(Zn) from Dobšiná.*

Table 9 *Representative WDS analyses of tetrahedrite-(Zn) from Dobšiná (wt.%)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ag	0.23	0.16	0.17	0.24	0.09	0.16	0.19	0.20	0.19	0.18	0.21	0.15	0.14	0.17
Fe	1.34	1.30	1.74	1.90	1.52	1.72	1.72	2.67	1.96	1.68	2.33	2.82	1.99	2.01
Pb	0.00	0.08	0.08	0.11	0.00	0.00	0.07	0.09	0.08	0.14	0.00	0.10	0.00	0.07
Ni	0.28	0.41	0.00	0.00	0.00	0.00	0.00	0.44	0.15	0.00	0.00	0.00	0.00	0.00
Zn	5.88	5.96	4.94	4.73	5.29	5.01	5.22	4.04	5.08	5.38	4.29	4.00	4.75	4.79
Hg	0.37	0.21	0.24	0.44	0.24	0.20	0.38	0.31	0.16	0.37	0.30	0.38	0.50	0.37
Cu	37.76	37.83	38.93	39.19	39.40	39.18	39.29	38.74	39.15	39.34	39.77	38.98	39.99	40.26
Sb	29.35	28.98	29.15	28.95	28.85	28.16	27.10	26.43	26.22	26.03	24.17	24.17	22.75	22.41
As	0.11	0.26	0.31	0.39	0.43	0.76	1.57	2.02	2.31	2.86	3.60	3.92	4.59	4.77
S	25.07	24.95	24.68	24.75	25.04	24.64	24.79	25.32	25.48	24.95	25.14	25.61	26.04	25.96
total	100.39	100.14	100.24	100.70	100.86	99.83	100.33	100.26	100.78	100.93	99.81	100.13	100.75	100.81
Ag	0.036	0.025	0.026	0.037	0.014	0.025	0.029	0.030	0.029	0.027	0.032	0.023	0.021	0.025
Fe	0.400	0.388	0.521	0.566	0.450	0.514	0.510	0.786	0.573	0.494	0.685	0.823	0.574	0.579
Pb	0.000	0.006	0.006	0.009	0.000	0.000	0.006	0.007	0.006	0.011	0.000	0.008	0.000	0.005
Ni	0.079	0.116	0.000	0.000	0.000	0.000	0.000	0.123	0.042	0.000	0.000	0.000	0.000	0.000
Zn	1.498	1.520	1.263	1.204	1.338	1.280	1.324	1.016	1.269	1.352	1.077	0.998	1.170	1.178
Hg	0.031	0.017	0.020	0.036	0.020	0.017	0.031	0.025	0.013	0.030	0.025	0.031	0.040	0.030
Cu	9.896	9.926	10.235	10.261	10.252	10.297	10.248	10.021	10.064	10.167	10.270	10.003	10.130	10.185
Σ	11.939	11.999	12.071	12.114	12.074	12.133	12.148	12.009	11.997	12.082	12.088	11.885	11.934	12.002
Sb	4.015	3.969	4.000	3.956	3.918	3.863	3.689	3.568	3.518	3.511	3.258	3.237	3.008	2.959
As	0.024	0.058	0.069	0.087	0.095	0.169	0.347	0.443	0.504	0.627	0.788	0.853	0.986	1.023
Σ	4.039	4.027	4.069	4.043	4.013	4.032	4.037	4.011	4.022	4.138	4.046	4.090	3.994	3.983
S	13.021	12.974	12.860	12.843	12.913	12.834	12.815	12.980	12.981	12.780	12.866	13.024	13.072	13.016

calculated empirical formulae are based on sum of 29 *apfu*

to 0.47 *apfu* and Sb up to 0.09 *apfu*. The similar variations in As/S ratio were observed by Kiefer et al. (2017) in other samples from Dobšiná and also by Ondruš et al. (2003) and Sejkora et al. (2015) in rammelsbergite from the Czech Republic.

Ullmannite is a relatively common mineral in the studied mineral association. It occurs as anhedral grains and aggregates up to 60 μm in size enclosed together with rammelsbergite in nickeline (Fig. 3) or with rammelsbergite and millerite in gersdorffite rims (Fig. 14).

The chemical composition of ullmannite from Dobšiná (Tab. 7) is close to the theoretical empirical formula NiSbS. Only minor amounts of Co (up to 0.01 *apfu*) and also Sn (0.09 to 0.17 wt. %; corresponding to 0.002 - 0.003 *apfu*) were observed in Me site. Besides Sb, slightly increased contents of As (ranging between 0.09 - 0.17 *apfu*, Fig. 11) are present as well. The mean (n=12) empirical formula of the studied ullmannite is $Ni_{1.00}(Sb_{0.88}As_{0.13})_{\Sigma 1.01}S_{0.99}$.

Millerite is rare. It forms anhedral grains and aggregates up to 50 μm in size, enclosed in gersdorffite rims in close association with ullmannite (Fig. 14). The chemical composition of millerite from Dobšiná (Tab. 8) is nearly stoichiometric, with only very minor amounts of Fe, Co, Cu, Pb, Sb and Te (all of them under the 0.01 *apfu*) present.

Tetrahedrite-(Zn) is common as anhedral grains and aggregates up to 1 cm enclosed in Fe-rich dolomite gangue. It is often intergrown with or rimmed by gersdorffite (Fig. 7, 8). Inclusions and veinlets of chalcopyrite and aggregates of bornite were locally observed in tetrahedrite-(Zn). Slight chemical zoning of tetrahedrite-(Zn) observed in BSE (Fig. 15, 17) is caused by variations in Sb and As contents. The relationship between tetrahedrite-(Zn) and nickeline is uncertain, because those two minerals occur always separately.

Table 10 *Chemical composition of chalcopyrite from Dobšiná (wt.%)*

	mean	1	2	3	4	5	6
Fe	27.90	27.53	28.10	28.06	27.68	28.12	27.91
Pb	0.10	0.10	0.11	0.14	0.10	0.09	0.08
Ni	0.47	0.34	0.29	0.22	0.69	0.56	0.72
Cu	34.60	34.60	34.58	34.58	35.17	34.40	34.27
Sb	0.57	0.91	0.54	0.73	0.22	0.53	0.48
S	34.87	34.52	34.86	34.82	35.06	35.13	34.85
total	98.52	98.00	98.48	98.55	98.92	98.83	98.31
Fe	0.932	0.927	0.939	0.938	0.919	0.935	0.933
Pb	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Ni	0.015	0.011	0.009	0.007	0.022	0.018	0.023
Cu	1.015	1.024	1.015	1.016	1.027	1.005	1.007
Sb	0.009	0.014	0.008	0.011	0.003	0.008	0.007
S	2.028	2.024	2.028	2.027	2.028	2.034	2.029

mean - average of 6 analyses; calculated empirical formulae are based on sum of 4 *apfu*

Representative quantitative chemical analyses of tetrahedrite-(Zn) are shown in Table 9. The trigonal position is predominantly occupied by Cu, with only minor amounts of Ag (up to 0.04 *apfu*). Zn is the prevailing element (ranging between 1.00 to 1.52 *apfu*) in the tetrahedral site accompanied by a range of other Me^{2+} cations (Fe up to 0.82, Ni up to 0.12, Hg up to 0.04 and Pb up to 0.01 *apfu*) and Sb is considerably prevailing (2.96 - 4.01 *apfu*, Fig. 16) over As (0.02 - 1.02 *apfu*), thus according to the recently published nomenclature scheme of minerals of the tetrahedrite group (Biagioni et al. 2020), the studied phase clearly corresponds to tetrahedrite-(Zn). The contents of S are ranging in 12.72 - 13.07 *apfu*.

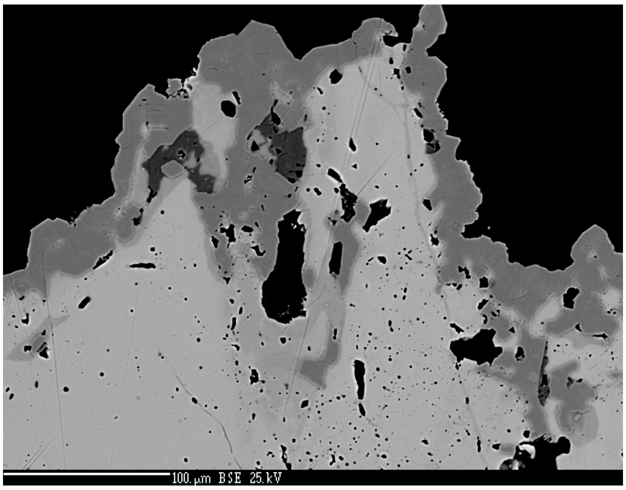


Fig. 17 *Anhedral grains of bornite (dark grey) are scattered along the boundary between the aggregate of tetrahedrite-(Zn) (light grey, with slight irregular zoning) and rim of gersdorffite (medium grey, type 3). BSE image by Z. Dolníček.*

Table 11 *Chemical composition of bornite from Dobšiná (wt.%)*

	mean	1	2	3	4	5	6
Ag	0.11	0.10	0.07	0.10	0.12	0.14	0.14
Fe	10.16	10.76	10.31	10.20	9.90	9.83	9.98
Pb	0.11	0.05	0.12	0.14	0.07	0.13	0.14
Ni	0.32	0.42	0.27	0.24	0.32	0.43	0.23
Zn	0.15	0.09	0.00	0.00	0.30	0.31	0.17
Hg	0.03	0.11	0.00	0.09	0.00	0.00	0.00
Cu	60.98	60.70	61.79	61.79	60.35	60.16	61.11
Sb	0.74	0.45	0.08	0.11	1.64	1.51	0.66
S	25.69	25.00	25.85	25.82	25.74	25.93	25.77
total	98.29	97.68	98.49	98.49	98.44	98.44	98.20
Ag	0.005	0.005	0.003	0.005	0.006	0.007	0.007
Fe	0.929	0.992	0.937	0.928	0.907	0.899	0.913
Pb	0.003	0.001	0.003	0.003	0.002	0.003	0.003
Ni	0.028	0.037	0.023	0.021	0.028	0.037	0.020
Zn	0.011	0.007	0.000	0.000	0.023	0.024	0.013
Hg	0.001	0.003	0.000	0.002	0.000	0.000	0.000
Cu	4.901	4.920	4.937	4.943	4.859	4.836	4.912
Sb	0.031	0.019	0.003	0.005	0.069	0.063	0.028
S	4.091	4.016	4.093	4.093	4.107	4.131	4.105

mean - average of 6 analyses; calculated empirical formulae are based on sum of 10 *apfu*

Chalcopyrite forms anhedral grains and veinlets up to 100 μm in size (Fig. 8), which are enclosed in tetrahedrite-(Zn). The analysed chalcopyrite from Dobšiná (Tab. 10) shows uncommon minor contents of Ni (up to 0.02 *apfu*) and Sb (up to 0.01 *apfu*), with a mean (n=6) empirical formula corresponding to $Cu_{1.02}(Fe_{0.93}Ni_{0.01})_{\Sigma 0.94}Sb_{0.01}S_{2.03}$.

Bornite is a minor mineral in the studied mineral association. It occurs as anhedral grains up to 40 μm in size, which are scattered along the boundary between the aggregate of tetrahedrite-(Zn) and gersdorffite rim (Fig. 17). The chemical composition of bornite from Dobšiná (Tab. 11) corresponds to the ideal formula Cu_5FeS_4. Only minor contents of Ni (up to 0.04 *apfu*) and Sb (up to 0.07 *apfu*) were determined. The mean composition of bornite (calculated from 6 analyses) is $Cu_{4.90}Ag_{0.01}Fe_{0.93}Ni_{0.03}Zn_{0.01}Sb_{0.03}S_{4.09}$.

Discussion and conclusions

The studied assemblage of Ni arsenides and sulfarsenides is represented by the abundant nickeline and gersdorffite with minor amounts of rammelsbergite and ullmannite. In general, nickeline is a rare mineral in the hydrothermal veins around Dobšiná as well as at the other siderite type veins in the Spišsko-gemerské rudohorie Mts. Halahyjová-Andrusovová (1957, 1959) described the presence of abundant nickeline only from the Tešnárky vein system. More recently Števko et al. (2013) discovered abundant nickeline associated with krutovite and galena in the carbonate-quartz vein hosted at the contact between serpentinite and limestone at the Dobšiná-Teliatko serpentinite body, but no occurrence of nickeline was reported from the Zemberg-Terézia vein system. Ullmannite and millerite were not yet reported from the veins in the Dobšiná area. The most interesting feature of the studied mineral association is the enrichment in Sb, which is highly unusual for the arsenides and sulfarsenides from Dobšiná. Both nickeline and gersdorffite contain significant amounts of antimony, which is in contrary with data published for gersdoffite from Dobšiná by Husár (1982), Flassiková (1991), Chovan (1995), Chovan, Ozdín (2003), Kiefer et al. (2017) and Kyrc (2019) or with the data published for nickeline by Števko et al. (2013). Another interesting aspect is that the tetrahedrite-(Zn) is overgrown by gersdorffite, because Cu minerals (tetrahedrite, chalcopyrite) tend to be always younger than the all arsenides and sulfarsenides (e.g. Halahyjová-Andrusovová 1957, 1959, 1964a; Kiefer et al. 2017; Kyrc 2019). Thus it is possible that at least locally, several generations of gersdorffite might be present. This theory is also supported by the fact that the chemical composition of those two paragenetic types of gersdorffite is different.

An interesting association of Sb-enriched Ni arsenides and sulfarsenides was discovered at the Zemberg-Terézia vein system near Dobšiná, Slovak Republic. The main ore minerals in this assemblage are nickeline and gersdorffite accompanied by rammelsbergite, ullmannite, millerite, tetrahedrite-(Zn), chalcopyrite and bornite.

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