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New data on sulfosalts from the hydrothermal siderite-type veins in the Spišsko-gemerské rudohorie Mts. (eastern Slovakia): 5. Minerals of the kobellite-tintinaite series from the Majerská dolina ore occurrence near Čučma

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Abstract

A new occurrence of minerals of the kobellite-tintinaite series was recently discovered at the Majerská dolina siderite-type hydrothermal ore occurrence near Čučma, Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Slovakia. Minerals of the kobellite-tintinaite series occur in quartz gangue as acicular to prismatic crystals up 5 mm long, associated together with arsenopyrite, pyrite and chalcopyrite. The calculated value of N for studied samples is ranging from 1.91 to 2.00 and the Sb/(Sb+Bi) atomic ratio in three studied samples varies between 0.41 and 0.52, hence corresponding mostly to Sb-rich kobellite, with a few analyses representing Bi-rich tintinaite.

Key words: *kobellite, tintinaite, kobellite homologous series, sulfosalts, chemical composition, siderite veins, Majerská dolina, Čučma, Spišsko-gemerské rudohorie Mts., Slovak Republic*

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Introduction

The Spišsko-gemerské rudohorie Mts. represent one of the most important accumulations of ore deposits in whole Carpathian mountain range. There are more than 1200 hydrothermal ore veins known within this relatively small area, with two major types of ore mineralization: siderite-type carbonate-quartz veins with sulfides (extensively exploited in Dobšiná, Štítnik, Rákoš, Rožňava, Drnava, Rudňany, Novoveská Huta, Hnilčík, Henclová, Prakovce, Gelnica, Slovinky, Medzev etc.) and quartz-stibnite veins (Betliar, Čučma, Bystrý potok, Štofova dolina, Helcmanovce, Poproč or Zlatá Idka). Furthermore, Sn-Mo-W bearing greisens or granite-related hydrothermal quartz veins, hydrothermal veins with U-REE mineralization as well as strata-bound VMS pyrite-Cu-Pb-Zn ore mineralization and hydrothermal-metasomatic bodies of siderite and magnesite±talc are present (Varček 1962; Chovan et al. 1994; Grecula et al. 1995; Rojkovič 1997). All of the abovementioned types of ore mineralization contain various sulfosalts mostly as accessory ore minerals.

Abundant presence of minerals of tetrahedrite-tennantite series (especially Fe, Zn and locally also Hg dominant members) is very typical feature of the siderite-type veins (e.g. Bernard 1958, 1961; Varček 1957, 1959, 1960; Novák 1959, 1967; Trdlička 1967; Háber 1980; Cambel et al. 1985; Peterec 1990; Miškovic 1991; Háber et al. 1993; Grecula et al. 1995; Antal 2002a, b; Pršek 2008; Pršek, Biroň 2007; Pršek, Lauko 2009; Števko et al. 2015; Mikuš et al. 2018; Peterec 2019; Števko, Sejkora 2020; Števko et al. 2022b). Various Bi sulfosalts are also quite common, especially minerals of the bismuthinite-aikinite series (e.g. Paděra et al. 1955; Kupčík et al. 1969; Hurný, Krištín 1978; Mumme, Žák 1983; Antal 1991; Macinský, Antal 1993; Beňka, Siman 1994; Pršek 2008; Števko et al. 2015; Mikuš et al. 2018, 2019; Števko et al. 2021a) and kobellite homologous series (e.g. Trdlička, Kupka 1957; Hak, Kupka 1958; Novák 1961; Trdlička et al. 1962; Václav 1964; Zábranský, Radzo 1966; Háber, Streško 1969; Háber 1980; Jeleň 1991; Pršek 2008; Pršek, Peterec 2008; Mikuš et al. 2018, 2019; Kúšik et al. 2021; Števko et al. 2021b, 2022a). Other Bi sulfosalts like cosalite (Bernard 1964; Háber 1980), galenobismutite (Antal 1991; Pršek 2008), jaskólskiite (Pršek, Biroň 2007; Števko et al. 2021b), nuffieldite (Pršek et al. 2006; Števko et al. 2021a) or wittichenite (Háber 1978; Kozub et al. 2011) are rare. Chalcostibite is infrequent too (Sejkora et al. 2011; Mikuš et al. 2018). Unusual assemblage of Ag-Bi sulfosalts (matildite, gustavite and benjaminite) was recently described from the Kobaltová vein near Medzev by Mikuš et al. (2019). The most common Pb sulfosalts at the siderite-type veins are bournonite, jamesonite (often Bi-rich) and boulangerite (e. g. Zimányi 1914; Novák 1962; Trdlička 1967; Kupčík et al. 1969; Varček 1971; Háber 1980; Miškovic 1990; Pršek, Biroň 2007; Pršek, Peterec 2008; Sejkora et al. 2011; Mikuš et al. 2018, 2019; Števko et al. 2021b, 2022a), whereas berthierite and garavellite (Mikuš et al. 2018), meneghinite (Beňka, Siman 1994) or zinkenite and scainiite (Sejkora et al. 2011) are scarce. Rare Hg sulfosalts, marrucciite (Sejkora et al. 2011) and grumiplucite (Števko et al. 2015) were also recently identified. As-rich sulfosalts, seligmannite and jordanite, were described from the Zenderling deposit near Gelnica by Sejkora et al. (2011).

Pecho et al. (1981) reported elevated content of bismuth in the ore samples from the Majerská dolina ore occurrence and speculated that some Bi sulfosalts might be present. Our detailed mineralogical research confirmed the presence of minerals of the kobellite-tintinaite series at this locality and their compositional variation is discussed in this paper.

Geological setting

A small occurrence of hydrothermal ore mineralization is situated around 1.9 km NNE of the Čučma village in the Majerská dolina valley, Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Slovakia. Ore samples with sulfosalts were collected at the small dump of old exploration adit (Fig. 1). GPS coordinates (WGS84) of this dump are: 48.705200° N and 20.558578° E, 461 m a.s.l. This locality was rediscovered by Pecho et al. (1981) during the geological mapping focused on hydrothermal Sb deposits. Hydrothermal quartz-siderite vein at the Majerská dolina ore occurrence is hosted in Early Paleozoic rocks of the Gelnica group (the Gemeric Unit), represented in this area by phyllites of the Bystrý potok Formation (Pecho et al. 1981; Bajaník et al. 1984). The dominant gangue mineral is quartz accompanied by siderite and abundant sulfides, mainly pyrite, arsenopyrite and chalcopyrite (Pecho et al. 1981). Pecho et al. (1981) also mentioned elevated amounts of Bi and Co in ore samples from this locality.

Our detailed mineralogical study of ore samples from this locality confirmed a presence of zonal, Co (up to 2.32 wt.% of Co) and Sb-rich (up to 5.03 wt.% of Sb) arsenopyrite as a source of Co and minerals of the kobellite-tintinaite series as a source of Bi.

Fig. 1 *View of dump of exploration adit at the Majerská dolina ore occurrence. Photo by M. Števko, December 2019.*

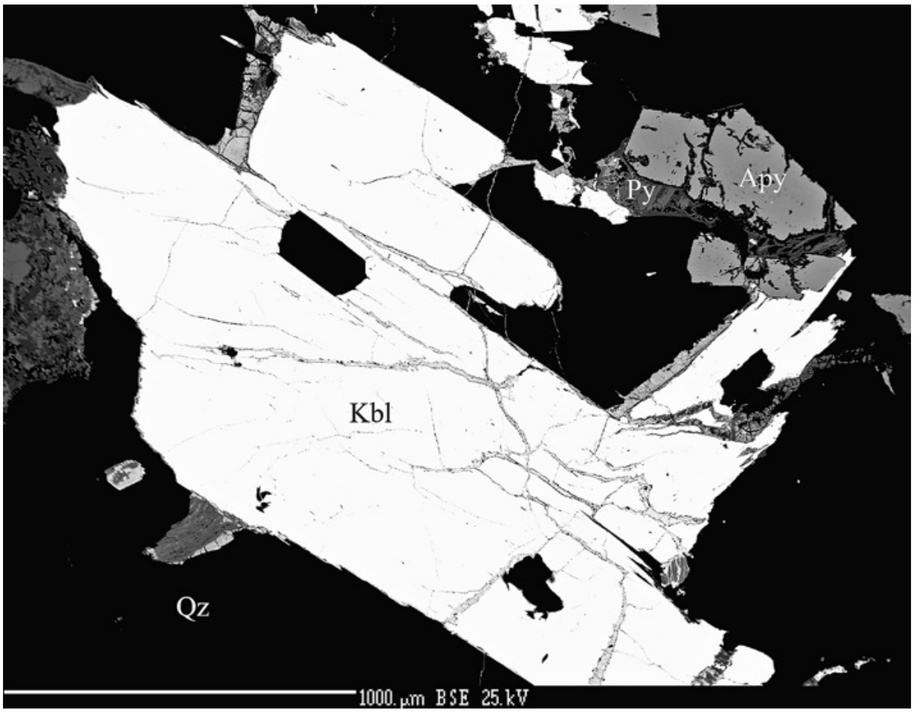

Fig. 2 *Aggregates of minerals of the kobellite-tintinaite series (Kbl) associated with arsenopyrite (Apy) and minor pyrite (Py) in quartz (Qz). Sample CM1, BSE image by J. Sejkora.*

Analytical methods

The quantitative chemical analyses of minerals of the kobellite-tintinaite series were performed using a Cameca SX100 electron microprobe (Department of Mineralogy and Petrology, 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 (Ag*L*α), Bi_2Se_3 (Bi*M*β), CdTe (Cd*L*α), Co (Co*K*α), $CuFeS_2$ (Cu*K*α, S*K*α), FeS_2 (Fe*K*α), GaAs (Ga*L*α), Ge (Ge*L*α), HgTe (Hg*L*α), InAs (In*L*α), Mn (Mn*K*α), NaCl (Cl*K*α), NiAs (As*L*β), Ni (Ni*K*α), PbS (Pb*M*α), PbSe (Se*L*β), PbTe

(Te*L*α), Sb_2S_3 (Sb*L*α), Sn (Sn*L*α), Tl(Br,I) (Tl*L*α), and ZnS (Zn*K*α). Contents of the above-listed elements, which are not included in the tables, were analysed quantitatively, but their contents were consistently 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 procedure (Pouchou, Pichoir 1985). The order number of kobellite homologue *N* was calculated according to the procedure proposed by Zakrzewski, Makovicky (1986).

Results

Minerals of the kobellite-tintinaite series are relatively rare at the studied locality. They form lead-grey, metallic, acicular to prismatic crystals up 5 mm long or aggregates of subhedral crystals (Fig. 2), enclosed in quartz together with pyrite, Co and Sb-rich arsenopyrite and minor chalcopyrite.

Representative quantitative chemical analyses of three samples of minerals of the tintinaite-kobellite series from the Majerská dolina ore occurrence and the corre-

Table 1 *Representative WDS analyses of minerals of the tintinaite-kobellite series from the Majerská dolina ore occurrence (wt. %)*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
sample	CM1	CM1	CM1	RM1	RM1	RM1	RM1	RM1	RM1	RM1	RM1	RM1	RM1	RM2	RM2
species	Kbl	Kbl	Kbl	Kbl	Kbl	Kbl	Tti	Kbl	Tti	Tti	Kbl	Kbl	Kbl	Kbl	Kbl
Pb	35.91	35.18	35.43	35.34	34.43	35.20	35.95	36.22	35.97	36.78	35.05	34.31	35.33	35.39	35.26
Ag	0.13	0.19	0.19	0.11	0.14	0.06	0.08	0.05	0.10	0.07	0.09	0.17	0.09	0.17	0.21
Cu	1.26	1.17	1.18	1.32	1.33	1.27	1.24	1.18	1.22	1.13	1.35	1.39	1.22	1.17	1.25
Fe	0.64	0.71	0.72	0.56	0.60	0.62	0.68	0.70	0.70	0.72	0.53	0.66	0.61	0.69	0.63
Sb	15.33	13.58	13.68	14.97	14.69	13.10	16.17	15.58	15.81	15.50	13.01	13.27	12.77	13.78	13.77
Bi	27.33	29.46	29.27	27.91	28.62	29.51	25.59	27.11	26.33	26.50	30.54	29.93	31.46	27.88	30.08
S	19.12	18.80	18.74	18.84	18.92	18.39	18.94	19.10	19.11	18.96	18.65	19.12	19.00	18.30	18.85
total	99.72	99.09	99.21	99.05	98.73	98.15	98.65	99.94	99.24	99.66	99.22	98.85	100.48	97.38	100.05
Pb	10.313	10.271	10.348	10.269	10.001	10.454	10.392	10.392	10.337	10.608	10.293	9.942	10.236	10.545	10.230
Ag	0.072	0.107	0.107	0.061	0.078	0.000	0.000	0.000	0.055	0.000	0.051	0.095	0.050	0.097	0.117
Σ	10.384	10.377	10.454	10.330	10.079	10.454	10.392	10.392	10.392	10.608	10.344	10.036	10.286	10.642	10.347
Cu	1.180	1.114	1.124	1.251	1.260	1.230	1.169	1.104	1.143	1.063	1.293	1.313	1.153	1.137	1.183
Fe	0.682	0.769	0.780	0.604	0.647	0.683	0.729	0.745	0.746	0.770	0.578	0.710	0.656	0.763	0.678
Σ	1.862	1.883	1.904	1.854	1.906	1.913	1.898	1.849	1.890	1.833	1.870	2.023	1.808	1.900	1.861
Bi	7.782	8.528	8.476	8.041	8.242	8.689	7.334	7.712	7.502	7.578	8.893	8.599	9.037	8.237	8.653
Sb	7.492	6.747	6.799	7.402	7.261	6.620	7.954	7.607	7.731	7.607	6.502	6.543	6.296	6.987	6.799
Σ	15.274	15.274	15.275	15.443	15.504	15.309	15.288	15.319	15.233	15.185	15.394	15.142	15.334	15.224	15.452
S	35.480	35.466	35.367	35.373	35.511	35.290	35.377	35.412	35.485	35.335	35.391	35.799	35.572	35.234	35.340
N	1.97	1.95	1.96	1.96	1.91	1.97	1.96	1.94	1.95	1.98	1.97	1.94	1.94	2.00	1.95
Sb/(Sb+Bi)	0.491	0.442	0.445	0.479	0.468	0.432	0.520	0.497	0.508	0.501	0.422	0.432	0.411	0.459	0.440

calculated empirical formulae are based on sum of all atoms = 63 *apfu*

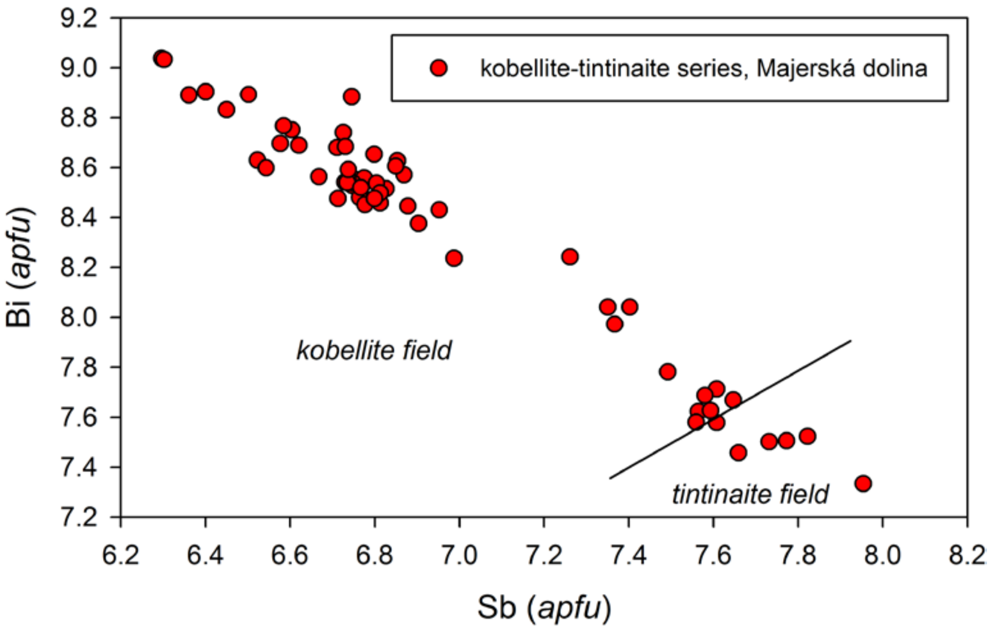

Fig. 3 *Variation of Sb vs. Bi contents (apfu) in minerals of the tintinaite-kobellite series from the Majerská dolina ore occurrence.*

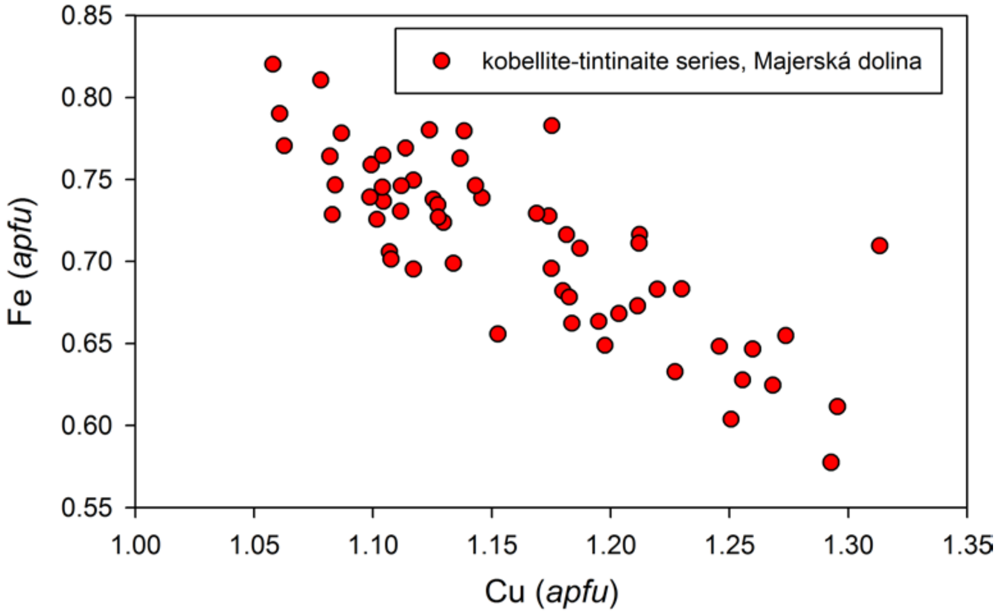

Fig. 4 *Variation of Cu vs. Fe contents (apfu) in minerals of kobellite-tintinaite series from the Majerská dolina ore occurrence.*

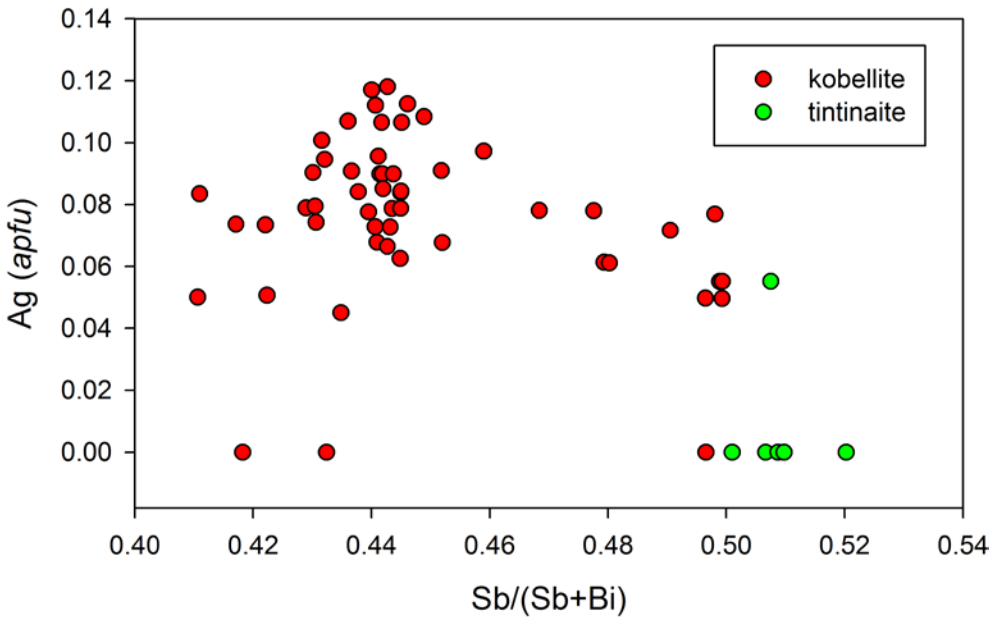

Fig. 5 *Graph of Sb/(Sb+Bi) ratio vs. Ag contents (apfu) in minerals of kobellite-tintinaite series from the Majerská dolina ore occurrence.*

sponding empirical formulae are shown in Table 1. All 59 WDS analyses are available as supplementary file. The calculated value of *N* (order number of kobellite homologue) for studied samples is ranging from 1.91 to 2.00 (with average of 1.95), which is close to the theoretical value *N* = 2 (e. g. Zakrzewski, Makovicky 1986; Moëlo et al. 1995, 2008). The Sb/(Sb+Bi) atomic ratio in samples from the Majerská valley ore occurrence varies between 0.41 and 0.52. The vast majority of analyses is corresponding to Sb-rich kobellite, with a few spots representing Bi-rich tintinaite (Fig. 3). The overall Cu+Fe content in studied samples of minerals of the kobellite-tintinaite series ranges from 1.81 to 2.02 *apfu* (with average of 1.87 *apfu*), which is close to the ideal value of 2 *apfu*. Variation of Cu and Fe contents in studied samples is shown in Figure 4. Furthermore, the minor presence of Ag (reaching up to 0.12 *apfu*) substituting for Pb was detected in studied samples; increased Ag contents were found especially in some Bi-rich members (Fig. 5).

Conclusions

A new occurrence of minerals of the kobellite-tintinaite series was discovered at the Majerská dolina ore occurrence near Čučma, Spišsko-gemerské rudohorie Mts., Slovakia. Studied samples show compositional variations between Sb-rich kobellite to Bi-rich tintinaite.

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