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PŮVODNÍ PRÁCE/ORIGINAL PAPER

New data on sulphosalts from the hydrothermal siderite-type veins in the Spišsko-gemerské rudohorie Mts. (eastern Slovakia): 3. Tintinaite and bournonite from the Gašpar (Grexa) vein near Rožňava

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Abstract

A new occurrence of tintinaite was recently discovered at the Gašpar (Grexa) siderite-type hydrothermal vein with sulphides located in the Rožňavská dolina valley near Rožňava, Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Slovakia. Tintinaite occurs as lead-gray, acicular to prismatic crystals up to 4 cm long or rich fibrous aggregates and nests reaching up to 7 × 5 cm, which are enclosed in quartz-siderite gangue. Crystals and aggregates of tintinaite are often directly associated with massive accumulations of older sulphides, especially arsenopyrite, chalcopyrite, pyrrhotite and pyrite. Grains and aggregates of younger native bismuth or bournonite are occasionally replacing aggregates of tintinaite. The refined unit-cell parameters of tintinaite (for the orthorhombic space group *Pnmm*) are: *a* 22.523(7) Å, *b* 34.137(11) Å, *c* 4.0389(14) Å and *V* 3105.4(1) Å³. The calculated value of *N* for tintinaite from the Gašpar vein is ranging from 1.93 to 2.00 and the Sb/(Sb+Bi) atomic ratio in three studied samples varies between 0.49 and 0.60, corresponding to Bi-rich tintinaite, with only one spot representing Sb-rich kobellite. The average Cu+Fe content in tintinaite is 1.96 *apfu* and minor concentrations of Ag (up to 0.14 *apfu*) and Se (up to 0.22 *apfu*) were also detected. The average (*n* = 55) empirical formula of tintinaite based on sum of all atoms = 63 *apfu* is $(\text{Pb}_{10.56}\text{Ag}_{0.07})_{10.63}(\text{Cu}_{1.12}\text{Fe}_{0.85})_{1.97}(\text{Sb}_{8.50}\text{Bi}_{6.75})_{15.25}(\text{S}_{35.01}\text{Se}_{0.15})_{35.16}$. Bournonite is rare and it forms anhedral grains or aggregates up to 220 μm, which are replacing aggregates of tintinaite. Its average (*n* = 8) empirical formula of bournonite based on sum of all atoms = 6 *apfu* is $\text{Pb}_{0.99}\text{Cu}_{1.00}(\text{Sb}_{0.98}\text{Bi}_{0.03})_{1.01}(\text{S}_{2.99}\text{Se}_{0.01})_{3.00}$.

Key words: tintinaite, kobellite homologous series, bournonite, sulphosalts, X-ray powder data, chemical composition, siderite veins, Gašpar vein, Grexa, Rožňava, 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 mineralization: siderite-type carbonate-quartz veins with sulphides (extensively exploited in Dobšiná, Štítnik, Rákoš, Rožňava, Drnava, Rudňany, Novoveská Huta, Hnilčík, Henclová, Prakovce, Gelnica, Slovinky, Medzev etc.) and quartz-stibnite veins (Betliar, Čučma, 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 above mentioned types of ore mineralization contain various sulphosalts 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; Števkó et al. 2015; Mikuš et al. 2018; Peterec 2019; Števkó, Sejkora 2020). Various Bi sulphosalts are also quite common, especially minerals of the bismuthinite-aikininite series (e.g. Paděra et al. 1955; Kupčík et al. 1969; Hurný, Krištín 1978; Mumme, Žák 1983; Antal 1991; Beňka, Siman 1994; Pršek 2008; Števkó et al. 2015; Mikuš et al. 2018, 2019; Števkó et al. 2021a) and kobellite homologous series (e.g. Trdlička, Kupka 1957; Hak, Kupka 1958; Novák 1961; Trdlička et al. 1962; Václav 1964; Zábanský, Radzo 1966; Háber, Streško 1969; Háber 1980; Jeleň 1991; Pršek 2008; Pršek, Peterec 2008; Mikuš et al. 2018, 2019; Kúšik et al. 2021; Števkó et al. 2021b). Other Bi sulphosalts 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 sulphosalts (matildite, gustavite and benjaminite) was recently described from the Kobaltová vein near Medzev by Mikuš et al. (2019). The most common Pb sulphosalts at the siderite-type veins are bournonite, jamesonite (often Bi-rich) and boulangerite (e.g. Zimányi 1914; Novák 1962; Trdlička 1967; Kupčik et al. 1969; Varček 1971; Háber 1980; Miškovic 1990; Pršek, Biroň 2007; Pršek, Peterc 2008; Sejkora et al. 2011; Mikuš et al. 2018, 2019;

Števko et al. 2021b), whereas berthierite and garavellite (Mikuš et al. 2018), meneghinite (Beňka, Siman 1994) or zinkenite and scainiite (Sejkora et al. 2011) are scarce. Rare Hg sulphosalts, marrucciite (Sejkora et al. 2011) and grumiplucite (Števko et al. 2015) were also recently identified. As-rich sulphosalts, seligmannite and jordanite were described from the Zenderling deposit near Gelnica by Sejkora et al. (2011).

The occurrence of Bi sulphosalts at the Gašpar (Grexa) vein was first reported by Kupčik et al. (1969). They identified them as "rezbanyite", even though their published microprobe analyses are clearly corresponding to minerals of the kobellite-tintinaite series. Later, Biroň (1989) mentioned occurrence of kobellite at the Gašpar vein in his diploma thesis. This paper is presenting new compositional data on tintinaite and bournonite from this locality.

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Geological setting

The Gašpar vein (also known as Grexa vein) is located on NW slopes of the Tohajska hill (855 m a.s.l.), around 8 km NE of the Rožňava town in the Rožňavská dolina valley, Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Slovakia. Fragments and blocks of ore mineralization with abundant sulphides are very common at the dumps of both exploration adits. Very rich samples of ore mineralization with tintinaite were collected especially at the dump of lower exploration adit (Fig. 1). GPS coordinates (WGS84) of this dump are: 48.716317° N and 20.601933° E, 674 m a.s.l.

The Gašpar (Grexa) vein is one of the less important siderite-type hydrothermal veins belonging to the Rozgang vein system. It was explored by two adits, probably in the late 18th or early 19th century. This short, ENE-WSW trending hydrothermal vein is hosted in Early Paleozoic rocks of the Gelnica group (the Gemeric Unit), represented in this area by metasandstones and phyllites of the Bystrý potok Formation (Bajaník et al. 1984; Grecula et al. 1995). The estimation of the vein thickness based on the samples from the dumps is 30 cm. The dominant gangue minerals are siderite and quartz accompanied by minor amounts of ankerite, muscovite, rutile and minerals of the chlorite group. Sulphidic ore mineralization is quite common and it is represented by abundant aggregates and masses of arsenopyrite, chalcopyrite, pyrite, pyrrhotite, sphalerite, marcasite, bismuth sulphosalts ("rezbanyite", kobellite, tintinaite) and minor amounts of microscopic native bismuth (Kupčik et al. 1969; Biroň 1989; Grecula et al. 1995).



Fig. 1 View of the dump of the lower exploration adit. Photo by M. Števko, March 2020.



Fig. 2 Aggregates of tintinaite enclosed in quartz with accumulations of pyrite, pyrrhotite and minor arsenopyrite. Size of specimen is 7 × 6 cm. Photo by L. Vrtiška.

Analytical methods

The powder X-ray diffraction data of tintinaite were collected on a Bruker D8 Advance diffractometer (National Museum, Prague, Czech Republic) with a solid-state 1D LynxEye detector using CuK α radiation and operating at 40 kV and 40 mA. The powder patterns were collected using Bragg-Brentano geometry in the range 3 - 70° 2 θ , in 0.01° steps with a counting time of 8 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated values of intensities obtained from the crystal structure of kobellite (Miehe 1971), based on Lazy Pulverix program (Yvon et al. 1977).

The quantitative chemical analyses of tintinaite and bournonite 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 μ m wide beam). The following standards and X-ray lines were used to minimize line overlaps: Ag (AgL α), Bi₂Se₃ (BiM β), CdTe (CdL α), Co (CoK α), CuFeS₂ (CuK α , SK α), FeS₂ (FeK α), GaAs (GaL α), Ge (GeL α), HgTe (HgL α), InAs (InL α), Mn (MnK α), NaCl (ClK α), NiAs (AsL β), Ni (NiK α), PbS (PbM α), PbSe (SeL β), PbTe (TeL α), Sb₂S₃ (SbL α), Sn (SnL α), Tl-

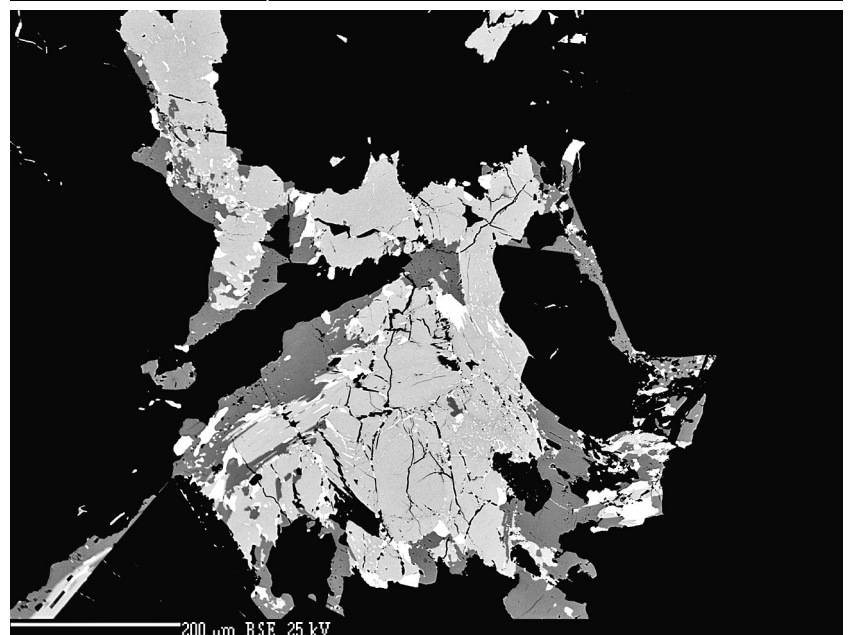
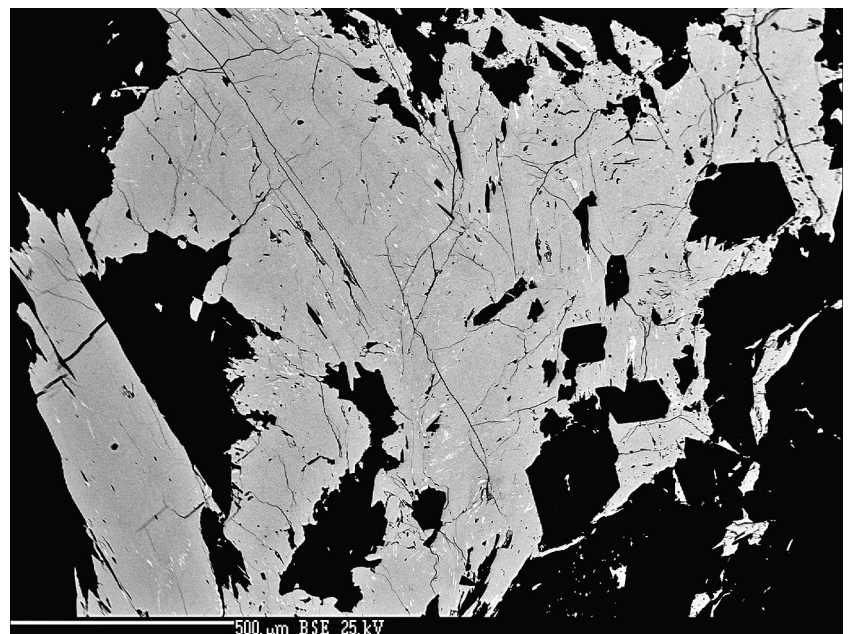
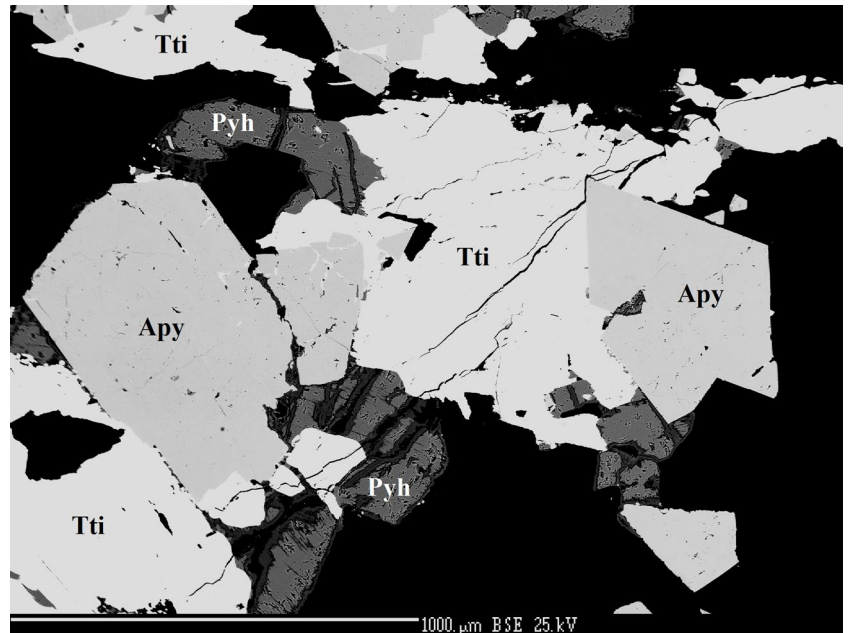


Fig. 3 Arsenopyrite crystals (Apy) overgrown by tintinaite aggregates (Tti) and subhedral grains of pyrrhotite (Pyh). BSE image by M. Števkó.

Fig. 4 Homogenous aggregates of tintinaite (light grey) with tiny inclusions of native bismuth (white). BSE image by M. Števkó.

Fig. 5 Aggregates of bournonite (dark grey) replace tintinaite (light grey). White inclusions are native bismuth. BSE image by M. Števkó.

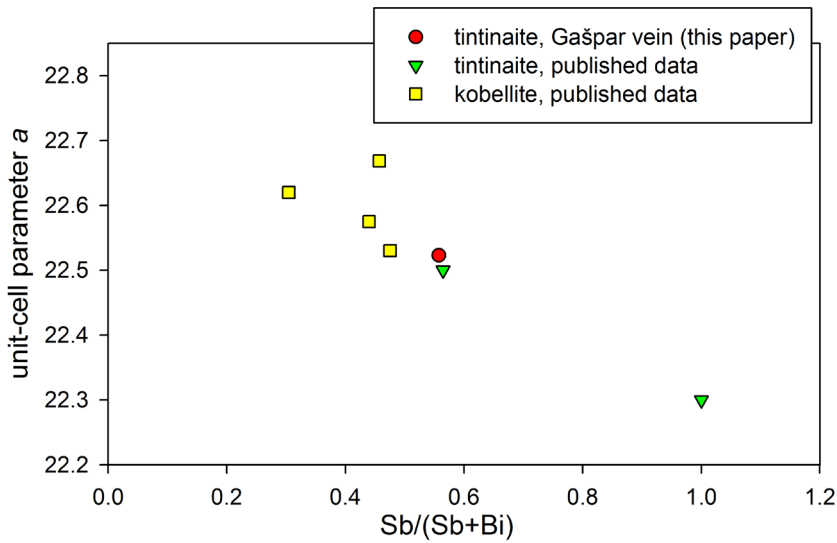
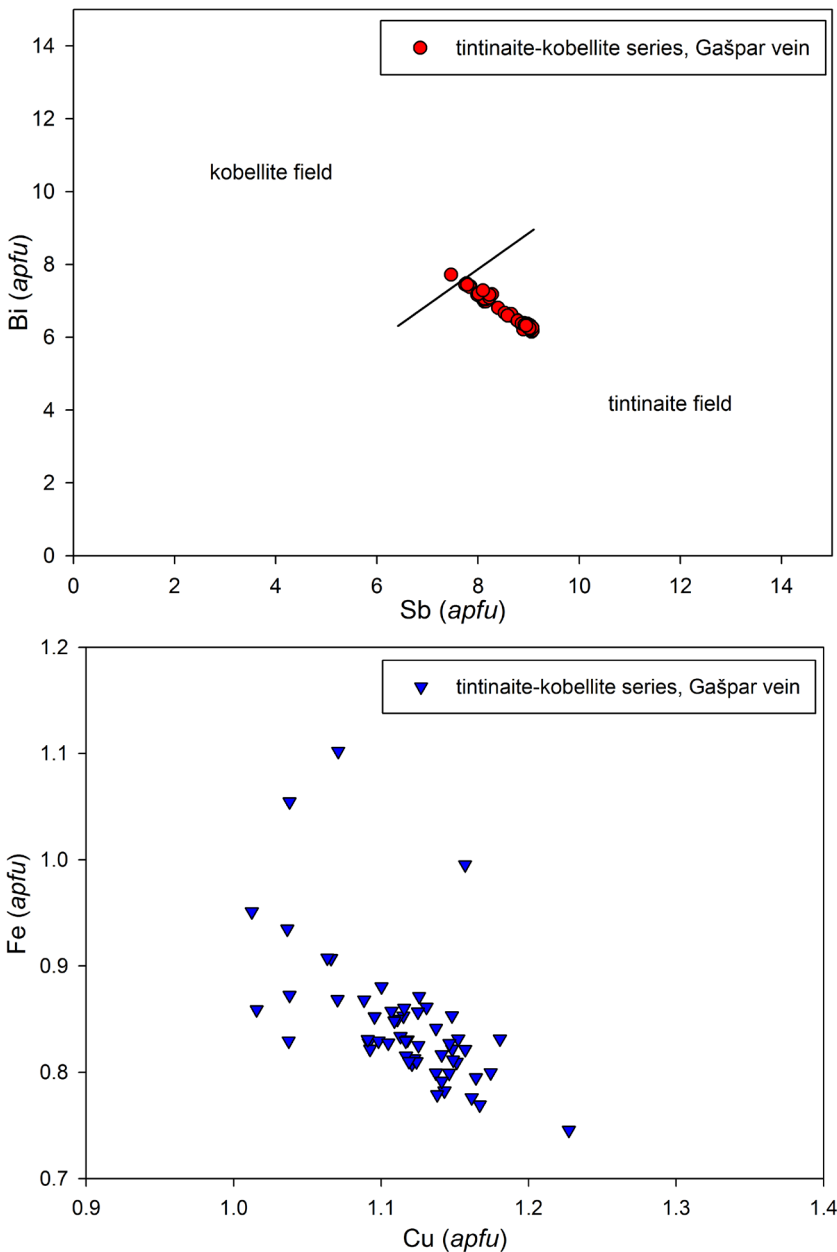


Fig. 6 Variation of unit-cell dimension a (in Å) vs. $Sb/(Sb + Bi)$ ratio (apfu) in minerals of the tintinaite-kobellite series; published data are taken from Table 2.



BrI (Tl α), and ZnS (ZnK 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 for tintinaite was calculated according to the procedure proposed by Zakrzewski, Makovicky (1986).

Results

Tintinaite is common mineral at the studied locality. It forms lead-grey, metallic, individual acicular to prismatic crystals up to 4 cm long or rich fibrous aggregates and nests reaching up to 7 × 5 cm (Fig. 2), enclosed in siderite or quartz. Tintinaite is often directly associated with massive accumulations of older sulphides, especially arsenopyrite, chalcopyrite, pyrrhotite and pyrite (Fig. 3). Aggregates of tintinaite are chemically very homogenous in BSE (Fig. 4) and are frequently containing minute inclusions of native bismuth. Tintinaite is also locally replaced by younger aggregates of bourmonite (Fig. 5).

The obtained experimental X-ray powder diffraction data set of tintinaite from the Gašpar vein given in Table 1 agrees well with published data for tintinaite and kobellite; the similarity of the crystal structures of these minerals and the wide range of $SbBi_{1-x}$ substitution do not allow their quick determination on the basis of PXRD. The refined unit-cell parameters of studied tintinaite are compared in Table 2 with published data for tintinaite and kobellite; the values of unit-cell parameter a distinctly negatively correlate with Sb contents (Fig. 6).

Representative quantitative chemical analyses of three samples of minerals of the tintinaite-kobellite series from the Gašpar vein and the corresponding empirical formulae are shown in Table 3. All 56 WDS analy-

Fig. 7 Variation of Sb vs. Bi contents (apfu) in minerals of the tintinaite-kobellite series from the Gašpar vein.

Fig. 8 Variation of Cu vs. Fe contents (apfu) in tintinaite from the Gašpar vein.

Table 1 X-ray powder diffraction data of tintinaite from the Gašpar vein

$l_{obs.}$	$d_{obs.}$	$d_{calc.}$	h	k	l	$l_{obs.}$	$d_{obs.}$	$d_{calc.}$	h	k	l	$l_{obs.}$	$d_{obs.}$	$d_{calc.}$	h	k	l
5.4	5.694	5.690	0	6	0	16.3	3.075	3.074	1	11	0	4.1	2.2504	2.2523	10	0	0
10.1	4.534	4.535	3	6	0	5.4	3.021	3.016	3	6	1	15.5	2.1565	2.1606	2	13	1
8.2	4.345	4.344	4	5	0	10.9	2.993	2.996	5	1	1	13.6	2.1277	2.1273	9	0	1
11.7	4.268	4.267	0	8	0	25.0	2.974	2.975	6	7	0	5.7	2.1099	2.1126	3	13	1
13.9	4.197	4.193	1	8	0	16.1	2.909	2.907	5	3	1	4.6	2.0897	2.0911	9	3	1
25.0	3.986	3.984	5	4	0	21.5	2.873	2.874	3	7	1	16.9	2.0458	2.0449	6	14	0
13.3	3.744	3.740	1	9	0	23.7	2.844	2.843	4	6	1	12.5	2.0334	2.0344	7	13	0
11.2	3.599	3.606	2	3	1	6.8	2.737	2.732	3	8	1	18.0	2.0178	2.0194	0	0	2
21.8	3.566	3.565	6	3	0	9.0	2.727	2.723	4	7	1	4.9	1.9803	1.9827	0	15	1
100.0	3.532	3.532	5	6	0	18.8	2.714	2.715	6	2	1	0.8	1.9762	1.9780	5	13	1
51.2	3.437	3.436	6	4	0	4.9	2.687	2.686	7	7	0	6.5	1.9534	1.9542	10	2	1
66.1	3.415	3.414	0	10	0	6.0	2.613	2.617	6	4	1	11.2	1.9295	1.9282	5	16	0
6.3	3.290	3.289	6	5	0	4.1	2.596	2.595	3	9	1	6.3	1.8519	1.8519	12	3	0
24.2	3.281	3.283	3	4	1	3.0	2.527	2.526	6	10	0	7.3	1.8066	1.8054	9	10	1
1.9	3.266	3.267	4	1	1	7.9	2.3604	2.3564	5	9	1	7.1	1.7899	1.7888	4	16	1
5.4	3.223	3.223	4	2	1	3.0	2.3128	2.3113	6	8	1	12.5	1.7525	1.7531	5	6	2
7.9	3.160	3.162	7	2	0	8.2	2.3043	2.3044	8	1	1	2.7	1.7436	1.7410	6	4	2
23.7	3.135	3.133	6	6	0	4.9	2.2726	2.2777	2	12	1	6.0	1.7384	1.7381	0	10	2
5.2	3.117	3.111	0	7	1												

Table 2 Unit-cell parameters of tintinaite (for orthorhombic space groups *Pnmm* and *Pnmm*)

tintinaite		Sb/(Sb+Bi)	a [Å]	b [Å]	c [Å]	V [Å ³]
Gašpar vein	this paper	0.557	22.523(7)	34.137(11)	4.0389(14)	3105.4(1)
Tintina	Harris et al. (1968)	1.000	22.30	34.00	4.04	3063.1
Rosslund	Harris et al. (1968)	0.565	22.50	34.00	4.03	3082.9
kobellite						
Korunka mine	Miehe (1971)	0.440	22.575(3)	34.104(4)	4.038(6)	3108.8
Raleigh	Harris et al. (1968)	0.475	22.53	33.97	4.04	3092.0
Salmo	Harris et al. (1968)		22.56	34.00	4.04	3098.8
Hvena	Nuffield (1948)	0.304	22.62	34.08	4.02	3099.0
Boliden mine	Mumme et al. (2013)	0.457	22.6686(6)	34.2577(7)	4.04091(8)	3138.1

Table 3 Representative WDS analyses of minerals of the tintinaite-kobellite series from the Gašpar vein (wt. %)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
sample	RV1	RV1	RV1	RV1	RV1	RV2	RV2	RV2	RV2	RV2	RV3	RV3	RV3	RV3	RV3
species	Tti	Kbl	Tti	Tti	Tti	Tti	Tti	Tti	Tti	Tti	Tti	Tti	Tti	Tti	Tti
Pb	36.89	36.26	36.71	37.09	37.11	37.96	37.35	37.07	36.97	36.10	37.16	37.51	37.17	37.02	37.63
Ag	0.16	0.19	0.12	0.17	0.00	0.12	0.14	0.14	0.26	0.17	0.15	0.09	0.18	0.11	0.10
Cu	1.24	1.23	1.11	1.21	1.15	1.16	1.23	1.15	1.09	1.17	1.18	1.21	1.24	1.33	1.22
Fe	0.81	0.93	0.82	0.77	0.86	0.87	0.74	1.04	0.81	0.82	0.78	0.79	0.76	0.71	0.83
Sb	17.38	15.21	15.87	16.52	16.68	18.02	18.08	16.71	16.47	16.04	18.65	18.80	18.38	18.41	18.68
Bi	24.16	26.98	26.19	25.57	25.44	23.64	22.91	24.92	25.38	26.31	22.27	21.92	22.59	22.71	22.30
S	19.13	18.75	18.96	19.05	19.11	19.22	19.00	18.88	18.98	19.09	19.06	19.16	19.13	19.21	19.09
Se	0.19	0.20	0.23	0.25	0.17	0.21	0.17	0.20	0.23	0.30	0.27	0.19	0.23	0.17	0.19
total	99.96	99.75	100.01	100.63	100.52	101.20	99.62	100.11	100.19	100.00	99.52	99.67	99.68	99.67	100.04
Pb	10.474	10.460	10.527	10.552	10.551	10.674	10.644	10.586	10.564	10.300	10.551	10.617	10.535	10.476	10.649
Ag	0.087	0.105	0.066	0.093	0.000	0.065	0.077	0.077	0.143	0.093	0.082	0.049	0.098	0.060	0.054
Σ	10.561	10.565	10.593	10.645	10.551	10.739	10.720	10.663	10.707	10.393	10.633	10.665	10.633	10.536	10.703
Cu	1.148	1.157	1.038	1.122	1.066	1.064	1.143	1.071	1.016	1.088	1.092	1.117	1.146	1.227	1.126
Fe	0.853	0.995	0.872	0.813	0.907	0.908	0.782	1.102	0.859	0.868	0.822	0.830	0.799	0.745	0.871
Σ	2.001	2.152	1.910	1.935	1.973	1.971	1.925	2.173	1.874	1.957	1.914	1.946	1.945	1.973	1.997
Sb	8.397	7.466	7.744	7.998	8.070	8.623	8.768	8.120	8.009	7.788	9.011	9.055	8.865	8.866	8.995
Bi	6.801	7.716	7.446	7.213	7.171	6.591	6.473	7.056	7.191	7.443	6.270	6.151	6.348	6.372	6.257
Σ	15.199	15.183	15.191	15.211	15.241	15.213	15.241	15.176	15.200	15.231	15.281	15.206	15.214	15.238	15.252
S	35.097	34.949	35.133	35.022	35.108	34.922	34.986	34.838	35.046	35.195	34.970	35.041	35.037	35.127	34.907
Se	0.142	0.151	0.173	0.187	0.127	0.155	0.127	0.150	0.172	0.225	0.201	0.141	0.171	0.126	0.141
Σ	35.239	35.100	35.306	35.208	35.234	35.077	35.114	34.988	35.219	35.420	35.172	35.182	35.208	35.254	35.048
N	1.97	1.96	1.96	1.99	1.93	1.97	2.00	1.95	1.99	1.94	1.97	1.98	1.99	1.98	1.97
Sb/(Sb+Bi)	0.55	0.49	0.51	0.53	0.53	0.57	0.58	0.54	0.53	0.51	0.59	0.60	0.58	0.58	0.59

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

Table 4 WDS analyses of bournonite from the Gašpar vein (wt. %)

	mean	1	2	3	4	5	6	7	8
Pb	41.58	41.67	41.91	41.83	41.31	40.99	41.29	41.90	41.78
Cu	12.91	12.98	12.77	13.01	12.84	12.99	13.12	12.71	12.89
Sb	24.40	24.25	24.44	24.60	24.42	24.17	24.16	24.62	24.58
Bi	1.33	1.59	1.25	1.13	1.30	1.61	1.41	1.21	1.14
S	19.58	19.34	19.33	19.25	19.94	19.99	20.01	19.54	19.26
Se	0.21	0.15	0.22	0.10	0.28	0.25	0.27	0.16	0.25
total	100.03	99.98	99.91	99.92	100.08	99.99	100.26	100.15	99.91
Pb	0.984	0.991	0.999	0.996	0.970	0.961	0.966	0.993	0.995
Cu	0.996	1.007	0.992	1.010	0.983	0.993	1.000	0.982	1.001
Sb	0.982	0.981	0.991	0.997	0.976	0.964	0.961	0.993	0.996
Bi	0.031	0.037	0.029	0.027	0.030	0.037	0.033	0.028	0.027
Σ	1.014	1.019	1.020	1.024	1.006	1.002	0.994	1.022	1.023
S	2.993	2.973	2.975	2.963	3.024	3.029	3.023	2.993	2.965
Se	0.013	0.010	0.014	0.006	0.017	0.016	0.017	0.010	0.016
Σ	3.007	2.983	2.989	2.969	3.042	3.044	3.040	3.003	2.980

calculated empirical formulae are based on sum of all atoms = 6 apfu

ses are available as supplementary file. The calculated value of N (order number of kobellite homologue) for tintinaite from the Gašpar vein is ranging from 1.93 to 2.00 (with average of 1.97), 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 Gašpar vein varies between 0.49 and 0.60. There is also only very minor variation of Sb vs. Bi contents between the individual samples. The vast majority of analyses are corresponding to Bi-rich tintinaite, with one spot representing Sb-rich kobellite (Fig. 7). The overall Cu + Fe content in tintinaite from the Gašpar vein ranges from 1.87 to 2.17 apfu (with average of 1.96 apfu), which is close to the ideal value of 2 apfu. Variation of Cu and Fe contents in studied samples is shown in Fig. 8. The content of Fe is relatively high (0.75 to 1.10 apfu). Similar or even slightly higher concentrations of Fe (up to 1.56 apfu) were reported by Mikuš et al. (2019) in tintinaite from the Oriješok vein near Medzev. Furthermore, the presence of Ag (reaching up to 0.14 apfu) substituting for Pb as well as stable presence of minor amounts of Se (up to 0.22 apfu) were detected in studied samples from the Gašpar vein. The average ($n = 55$) empirical formula of tintinaite based on sum of all atoms = 63 apfu is $(\text{Pb}_{10.56}\text{Ag}_{0.07})_{10.63}(\text{Cu}_{1.12}\text{Fe}_{0.85})_{1.97}(\text{Sb}_{8.50}\text{Bi}_{6.75})_{15.25}(\text{S}_{35.01}\text{Se}_{0.15})_{35.16}$.

Bournonite forms microscopic, anhedral grains or aggregates up to 220 μm (Fig. 5), which are replacing aggregates of older tintinaite. WDS analyses and corresponding calculated empirical formulae of bournonite from the Gašpar vein are shown in Table 4. Except for Pb, Cu, Sb and S as major constituents the studied bournonite has only minor contents of Bi (up to 0.04 apfu) and Se (up to 0.02 apfu). The average ($n = 8$) empirical formula of bournonite based on sum of all atoms = 6 apfu is $\text{Pb}_{0.99}\text{Cu}_{1.00}(\text{Sb}_{0.98}\text{Bi}_{0.03})_{1.01}(\text{S}_{2.99}\text{Se}_{0.01})_{3.00}$.

Conclusions

New samples of relatively rare Pb, Cu sulphosalt, tintinaite from the siderite-type hydrothermal carbonate-quartz Gašpar (Grexa) vein near Rožňava, Spišsko-gemerské rudohorie Mts., were studied in detail. Tintinaite is common mineral at this locality and it is associated with aggregates of older arsenopyrite, chalcopyrite, pyrrhotite and pyrite as well as inclusions of younger native bismuth. Bournonite is more rare and it is replacing aggregates of tintinaite.

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