

Original paper

# Tsumoite and associated tellurides from the Au deposit Libčice near Nový Knín, Czech Republic: mineralogy and genetic significance

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A mineral association with dominant pyrrhotite, tsumoite and gold, accompanied by minor tetradymite and pilsenite, has been found in material from the main vein of the abandoned Au deposit Libčice near Nový Knín, 25 km SSW of Prague, central Bohemia, Czech Republic. Tsumoite forms abundant silvery grey tabular aggregates up to 1–4 mm in size. The mineral is grey–white to very weakly beige-coloured in reflected light, anisotropic, with VHN microhardness 68 (63–76) kg/mm<sup>2</sup>, with  $K_{\text{VH}} = 1.21$ . Chemical analyses (electron microprobe) of matrix tsumoite yield Pb = 0.27, Cd = 0.12, Bi = 61.12, Te = 37.97, S = 0.01 and total of 99.50 wt. %, which corresponds to an empirical formula of  $\text{Bi}_{0.99}\text{Te}_{1.00}$  based on 2 *apfu*. The chemical composition of Bi-rich schlieren-like domains within the tsumoite is Pb 0.20, Cd 0.09, Bi 63.06, Te 36.44, S 0.01, total 99.80 wt. %, and corresponds to empirical formula  $\text{Bi}_{1.02}\text{Te}_{0.97}$  on the basis of 2 *apfu*. Both compositional varieties of tsumoite exhibit relatively small non-stoichiometry in Bi:Te ratio with respect to the ideal formula. The observed compositional range of tsumoite from Libčice corresponds to data published for this mineral species. Tsumoite is trigonal with space group *P*-3*m*1 and unit-cell parameters *a* 4.4204(9)–4.4210(8), *c* 24.043(7)–24.055(6) Å, *V* 406.9(1)–407.2(1) Å<sup>3</sup>. Pilsenite forms rare cleavable aggregates up to 80 μm. Its chemical composition Pb 0.09, Cd 0.12, Bi 67.63, Te 31.46, total 99.30 wt. % yields the empirical formula  $(\text{Bi}_{3.96}\text{Cd}_{0.01}\text{Pb}_{0.01})_{\Sigma 3.98}\text{Te}_{3.02}$  (based on 7 *apfu*). Younger tetradymite occurs in tiny irregular aggregates which partly overgrew and replaced tsumoite in association with native gold along fractures. The chemical composition of the tetradymite – Pb = 0.04, Cd = 0.11 Bi = 59.07, Te = 36.08, S = 4.50, total = 99.78 wt. % – corresponds to an empirical formula  $(\text{Bi}_{2.00}\text{Cd}_{0.01})_{\Sigma 2.01}\text{Te}_{2.00}\text{S}_{0.99}$  (based on 5 *apfu*). Associated pyrrhotite yielded formula  $\text{Fe}_{1-x}\text{S}$  with *x* values in the range 0.13–0.14. Gold contains low Ag (up to 4 wt. %) and Hg (up to 1 wt. %). The studied mineral association formed at elevated temperatures (>300 °C), probably at two stages differing in bismuth activity, as well as  $f_{\text{S}_2}$  and  $f_{\text{Te}_2}$  values. Alternatively, the two stages could have reflected variation of hydrothermal and metamorphic process in space and time.

**Keywords:** Bismuth-tellurides, tsumoite, X-ray powder diffraction data, chemical composition, Libčice gold deposit, Czech Republic

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## 1. Introduction

Bismuth-tellurides and Bi-sulphotellurides are characteristic accessory minerals of gold, gold-copper and base metal ore deposits of magmatic, hydrothermal and metamorphogenic type. The investigations of formation conditions and crystal chemistry (in particular the scope of possible non-stoichiometry and disorder character of crystal structure) brings information on ore genesis. For this reason, these minerals have been intensively studied recently (Gu et al. 2001; Ciobanu et al. 2006, 2009a; Cook and Ciobanu 2004; Cook et al. 2007a, 2007b; Parafiniuk et al. 2008; Tooth et al. 2008 and others).

Tsumoite, BiTe, first described in 1978 on material from the type-locality Tsumo Cu-Zn-Pb skarn deposit, Japan (Shimazaki and Ozawa 1978), belongs to the tetradymite group of Bi-tellurides. The main problem in nomenclature of minerals in the Bi–Te system relates to papers of Bayliss (1991), which presumed that there exists a

single solid-solution phase (Bi-rich tsumoite) with Bi and Te in proportions of 1.35 to 2.61. This presumption of the character of Bi-for-Te substitution has not been confirmed by new data. In difference to some other discontinuous solid solution series in the Bi–Te–Se–S system (Ciobanu et al. 2009b), tsumoite exhibits perfect stoichiometry in majority of occurrences or shows limited compositional variation with *c.* 42–50 at. % Te, corresponding to solid-solution of tsumoite phase in the binary system Bi–Te (Okamoto and Tanner 1990). According to Cook et al. (2007b), even in this narrow range there are several discrete phases (known from synthesis experiments), such as  $\text{Bi}_8\text{Te}_7$ ,  $\text{Bi}_{22}\text{Te}_{21}$ ,  $\text{Bi}_{32}\text{Te}_{33}$ ,  $\text{Bi}_{14}\text{Te}_{15}$ ,  $\text{Bi}_{26}\text{Te}_{29}$  and  $\text{Bi}_8\text{Te}_9$ , with 46.7, 48.8, 50.8, 51.7, 52.7 and 52.9 at. % Te. Broader solid-solution for tsumoite (exceeding the range of 42–50 at. % Te) has been described by Dobbe (1991) for Bi–Te compounds from Tunnaberg, Sweden, and by Cabri and Laflamme (1976) for “wehrlite” from Cu-Ni deposits of the Sudbury area, Canada. However, it

is probable that some of the chemical analyses published in these papers correspond to other minerals in the tetradyte group (e.g. hedleyite, pilsenite, unnamed Bi<sub>2</sub>Te etc.) (Cook et al. 2007b) or they may result from disorder on the lattice scale with nanoscale domains of structures with different composition (Ciobanu et al. 2009b).

Tsumoite occurrences in the Czech Republic have been described on the basis of energy dispersive microanalysis of microscopic aggregates (inclusions up to several µm across and microscopic intergrowth aggregates with other opaque minerals) in material from the gold deposits at Kašperské Hory (Scharmová and Pertoldová 1990) and Vacíkov–Petráčkova hora (Pertoldová and Šulcová 1994) as well as from the Zadní Chodov uranium deposit (Scharmová 1998). Tsumoite has also been described as inclusions up to 30 µm in size, in association with Pd minerals and native bismuth in Cu–Ni sulphide mineralization at Staré Ransko deposit (Vavřín et al. 1997; Vavřín and Frýda 1998; Pašava et al. 2003). The first occurrence in the Czech Republic of a macroscopic intergrowth of tsumoite with tetradyte and tellurobismutite was described by Litochleb et al. (2005) from gold-bearing quartz veins at Bytíz–Staré hory, near Příbram.

## 2. Geological setting

The Libčice deposit is situated on the eastern slopes of the Hořice hill west of Libčice, c. 4 km south of the town of Nový Knín in central Bohemia, Czech Republic. It represents a locality with the largest gold accumulation in the Nový Knín gold-bearing area with estimated historical production of two tons Au. Mining took place mainly during the Middle Ages, with the last activity during the first half of the 20<sup>th</sup> century. Workings reached a depth of nearly 200 m in the Middle Ages and belong thus, besides the Jílové gold-bearing district, to the deepest ones in Bohemia (Litochleb 1976, 2003). Exploration of deeper levels (from 300 to 400 m) started in 1945 and was terminated in 1957 (Malachov 1953; Havlíček 1959).

The deposit is located in the Dražetice volcanic body (dacite) of the Kozí Hory Belt and in tuffitic schists of Neoproterozoic age. At the eastern flank, and toward deeper levels, the intrusive body of the Variscan Libčice biotite granite of Central Bohemian Pluton limits the deposit and was responsible for its thermal metamorphism. Mineralization of the vein type is tied to steep lamprophyre dykes with two different trends. The main Libčice vein (known under historical name Mladá Kamlová Zone; Amort 1942) follows an east–west trending spessartite dyke. A second vein trend (Stará Kamlová Zone) accompanies north–south trending kersantite dykes. Both spessartite and kersantite dykes are older than ore mineralization and obviously than the Libčice biotite

granite (Morávek et al. 1992). These gold deposits are now considered examples of the so-called RIRG (reduced intrusion-related gold) type of gold deposits (Zachariáš et al. 2001). In contrast with other Au deposits of the Bohemian Massif, Au ore mineralization and surrounding rocks of the Libčice deposit were clearly thermally metamorphosed by the younger Libčice biotite granite.

The Libčice main vein with a steep dip of 75–90° to the north was opened at the level of seven galleries to a depth of nearly 400 m below surface. The main parts of the vein have been exploited to a depth of 200 m. The mineralized parts of the vein form a steep ore column 250–350 m long, bound at depth by the contact to the granite intrusion. In the east and west, the ore column is limited by wedging-out of the quartz vein and the host lamprophyre dyke. Shallow dip of the granite contact toward the west results in a wide zone of contact metamorphism of Neoproterozoic rocks and gold-bearing veins. The older age of the lamprophyre and gold-bearing vein is documented by the presence of their xenoliths in granite in a distance up to several metres from the contact (Pivec and Šrein 1987). The vein of massive grey–white quartz is on average 0.2–0.3 m wide, locally it exceeds 1 m. The content of ore minerals is variable, usually low. Gold of a high fineness is typically finely disseminated but it forms some local macroscopic aggregates. Gold content is highly variable, values of 10–270 g Au/t, locally up to as much as 1,000 g Au/t, were reported in old workings. There is a weak decline in the gold content with depth, but the width of veins is strongly reduced. The gold-bearing quartz vein is cut by flat lying dykes of aplite and pegmatite and disrupted by fractures trending N–S and E–W, often filled by calcite (with palygorskite) or rare galena with sphalerite (Morávek 1958).

The granular texture of vein quartz and the presence of contact metamorphic silicates (such as wollastonite, diopside and grossular–andradite) in mineralized quartz gangue indicate thermal recrystallization. The situation points to overprinting of hydrothermal products by magma-related thermal recrystallization and to specific minerogenetic conditions corresponding to epidote–amphibole or amphibole hornfels metamorphic facies.

Ore mineralization is characterized by abundant hexagonal pyrrhotite, less common pyrite, arsenopyrite and molybdenite, gold in two generations (gold I with 2–5 wt. % Ag and younger gold II with 12–13 wt. % Ag), and fine-grained aggregates of Bi–tellurides (Malec et al. 1985; Litochleb and Šrein 1994; Šrein et al. 1995). Zachariáš et al. (1997) proposed the following crystallization succession: quartz I, pyrrhotite → arsenopyrite I, pyrite I → loellingite → gold, Bi–tellurides, calcite I → quartz II, (Co-) arsenopyrite II, pyrite II, gold II, CoSbS → pyrrhotite, chalcopyrite, tetrahedrite → pyrite III, calcite II, quartz III.

Previous studies at this deposit resulted in the description of several minerals belonging to the Bi-tellurides group. Slavik (1918) reported occurrences of so-called tellurobismuthite (rich finds at the third level). Besides that were identified tetradymite, joséite B (Šrein et al. 1995) and silvery white tabular crystals, ascribed, without compositional data, to 'wehrlite' (Sobotka 1959), later re-defined as pilsenite (Ozawa and Shimazaki 1982). The occurrence of Au and Ag tellurides, reported by Hofmann (1912), has not been confirmed by subsequent studies. According to Malec et al. (1985), these minerals most likely represent microscopic intergrowths of gold with Bi-tellurides.

### 3. Analytical techniques

Polished sections of the studied samples from Libčice were prepared for optical investigation, measurement of microhardness and chemical analysis using standard diamond polishing techniques. Optical properties in reflected light were observed with a Nikon Eclipse ME600 microscope. The Vickers microhardness of tsumoite was measured using a PMT-3 instrument with 15g load (calibrated on halite crystal with 5g load, indenter exposure 15 s, average value was calculated from 20 measurements on three grains).

Back-scattered electron (BSE) images were acquired and quantitative chemical compositions of minerals determined with a Cameca SX100 electron microanalyzer (Faculty of Science, Brno) operated at the following conditions: wave-length dispersive analysis, 25 kV, 20 nA, electron beam diameter less than 1  $\mu\text{m}$ . The following standards were used: Ag ( $\text{AgL}_\alpha$ ), Au ( $\text{AuL}_\alpha$ ), Bi ( $\text{BiM}_\beta$ ),  $\text{Bi}_2\text{Te}_3$  ( $\text{TeL}_\beta$ ), CdTe ( $\text{CdL}_\beta$ ), chalcopyrite ( $\text{SK}_\alpha$ ), Cu ( $\text{CuK}_\alpha$ ),  $\text{FeS}_2$  ( $\text{FeK}_\alpha$ ), pararammelsbergite ( $\text{AsL}_\beta$ ),  $\text{PbCl}_2$  ( $\text{ClK}_\alpha$ ),  $\text{PbSe}$  ( $\text{PbM}_\alpha$ ,  $\text{SeL}_\beta$ ) and Sb ( $\text{SbL}_\beta$ ). The abundances of the above elements, if not included in analytical data tables, were measured, but the values were below the respective detection limit (0.01–0.03 wt. % for individual elements). Measured data were corrected using the PAP software (Pouchou and Pichoir 1985).

A handpicked sample of tsumoite was used for powder X-ray diffraction experiments. The continuous mode of the PANalytical X'Pert Pro powder diffractometer (Faculty of Science, Charles University, Prague) operating at 40 kV and 40 mA with X'Celerator detector was used. Firstly, the sample was measured at Bragg-Brentano geometry. The sample studied was placed onto the surface of a flat silicon monocrystal wafer from the suspension of acetone in order to minimize complicated background. The X-ray powder diffraction data were collected from  $3^\circ$  to  $75^\circ 2\theta$  with integrated step of  $0.02^\circ 2\theta$  and virtual time per integrated step of 350 seconds. Later, small amount

of sample powder was mounted on a thin glass fibre onto goniometric head and scanned in Debye-Scherrer's geometry. For unit-cell parameters the powder X-ray diffraction pattern was collected in the range of  $6\text{--}75^\circ 2\theta$  with  $\text{CuK}\alpha$  radiation (Ni-filter, integrated step  $0.02^\circ 2\theta$ , virtual time 2500 s, sample was rotated). In both cases, the position of each diffraction maxima was refined using profile shape function Pearson VII by software ZDS (Ondruš 1993) and was used for unit-cell parameter refinement by software of Burnham (1962) based on least-squares method.

## 4. Results and discussion

### 4.1. Sample description

The several studied samples were collected in 1955 on the 5<sup>th</sup> level of the Libčice mine in the main vein of the deposit, west of the shaft, near the contact with the Libčice granite. The samples represent a fine-grained black–green, hornfels-like rock with nearly massive grey quartz, and showing slickenside surfaces. The rock contains irregular granular sulphide aggregates (pyrrhotite, pyrite, arsenopyrite) 0.X to 5–10 mm in size, fine-grained deep yellow gold and abundant silvery to light yellowish flaky tsumoite aggregates 1–4 mm across. Bi-tellurides, gold and sulphides form mutual intergrowths.

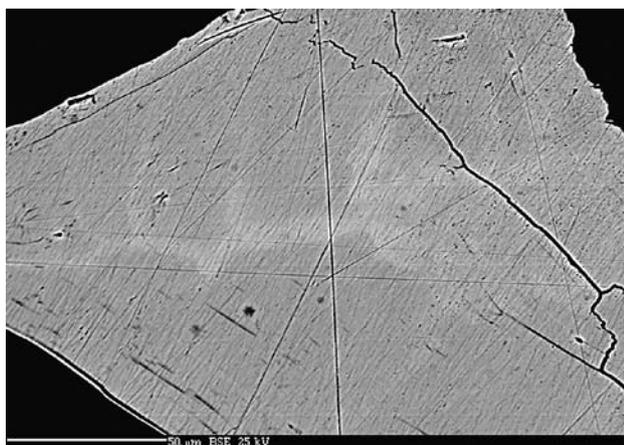
### 4.2. Tsumoite

Tsumoite is by far the most abundant Bi telluride in the studied mineral association. Some parts of the samples contain tsumoite in amounts comparable to the most abundant sulphide – pyrrhotite. Tsumoite forms irregular platy aggregates 1–4 mm long, showing a weak cleavage. On fresh fracture the mineral has an imperfect and silvery white metallic lustre. Compared to other Bi tellurides (tetradymite, tellurobismuthite etc.) it is clearly darker. In reflected light tsumoite is grey–white with a weak creamy shade, under crossed polarizers it is weakly anisotropic and shows grey–brown colour effects.

Vickers microhardness  $\text{VHN}_{15\text{g}} = 68$  (63–76)  $\text{kg/mm}^2$  with anisotropy coefficient  $K_{\text{VH}} = 1.21$  was measured on the studied tsumoite. There are few such published data on tsumoite microhardness, because of the generally very fine grain size of the mineral. Shimazaki and Ozawa (1978) reported values 51–90  $\text{kg/mm}^2$ , Pavlova et al. (1988) measured on tsumoite from  $\text{BiTe-Bi}_3\text{S}_5$  decomposition structures  $\text{VHN}_{20\text{g}} = 101$  (93–108)  $\text{kg/mm}^2$ . This value is influenced by higher hardness of the intimately intergrown phase  $\text{Bi}_3\text{S}_5$ . Litochleb et al. (2005) reported  $\text{VHN}_{15\text{g}} = 109$  (93–133)  $\text{kg/mm}^2$  with anisotropy

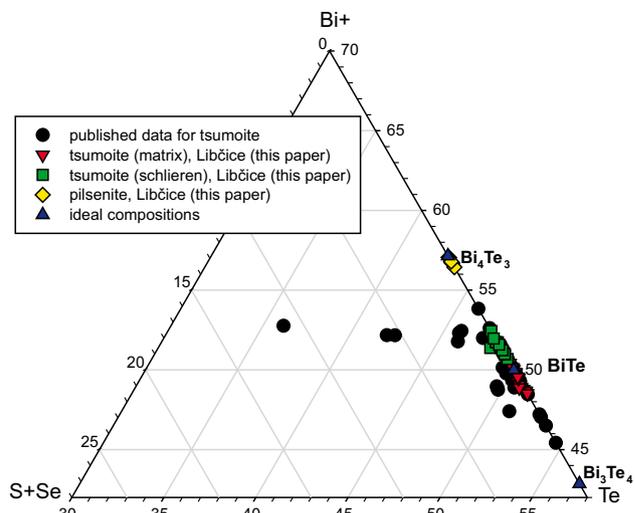
coefficient  $K_{VH} = 1.43$ . The differences in measured microhardness of tsumoite from the localities Bytíz–Staré hory (Litochleb et al. 2005) and Libčice (this study) relate to hardness anisotropy of the second order (reticular anisotropy) in sections with different crystallographic orientations. In sample from Libčice were measured sections approximately normal to the basal plane, showing lower microhardness, whereas that from Bytíz–Staré hory was cut nearly parallel to the basal plane. The measured values indicate that tsumoite shows usually a higher microhardness in comparison with other phases in the Bi–Te–S system.

A detailed examination of the BSE images resulted in the recognition of irregular schlieren-like domains in parts of tsumoite aggregates (Fig. 1). A lighter Bi-rich phase



**Fig. 1** A BSE image of irregular schlieren of lighter Bi-rich tsumoite passing gradually, without a clear boundary, into a matrix of darker tsumoite.

of the schlieren passes gradually, without clear boundary, into darker Bi-poor matrix. Quantitative chemical analyses (Tab. 1) show that the tsumoite matrix (Figs 2–3) has the average Bi:Te ratios 0.99 (0.94–1.04) and Te contents of 50.3 (48.5–51.5) at. %. The empirical formula for matrix tsumoite (average of 27 spot analyses) is  $Bi_{0.99}Te_{1.00}$ , based on 2 *apfu*, i.e. perfect stoichiometry within the range of analytical error. The lighter schlieren with Bi:Te ratio 1.06 (1.03–1.10) and 48.5 (47.5–49.2) at. % Te represent Bi-rich variant of tsumoite with empirical formula

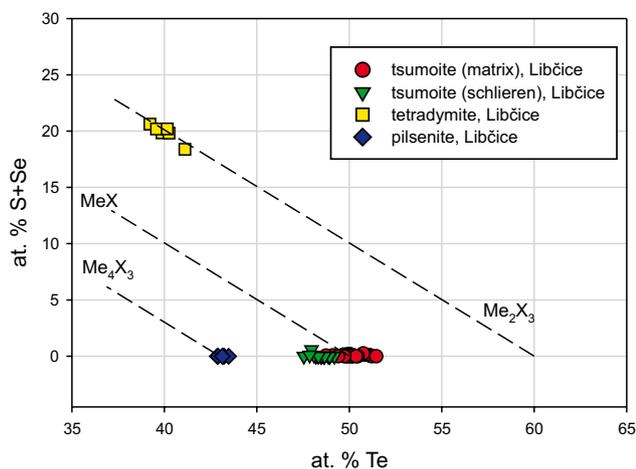


**Fig. 2** Part of Bi+ vs Te vs S + Se ternary plot for Bi tellurides from Libčice. Bi+ = Bi + Sb + Pb + Cd + Ag + Fe + Cu + Hg; published data for tsumoite are taken from papers of Shimazaki and Ozawa (1978), Zavalov et al. (1978), Gamjanin et al. (1980), Gu et al. (2001), Cook and Ciobanu (2004), Ferenc (2004) and Litochleb et al. (2005).

**Tab. 1** Representative chemical composition of two types of tsumoite from Libčice near Nový Knín (wt. %). Number of atoms based on 2 *apfu*

	tsumoite – matrix							tsumoite – schlieren						
	mean* (n = 27)*	range	1	2	3	4	5	mean* (n = 14)*	range	1	2	3	4	5
Pb	<b>0.27</b>	0.09–0.52	0.43	0.27	0.18	0.23	0.15	<b>0.20</b>	0.14–0.32	0.01	0.24	0.32	0.27	0.16
Cd	<b>0.12</b>	0.03–0.36	0.03	0.15	0.15	0.07	0.36	<b>0.09</b>	0.02–0.18	0.18	0.11	0.12	0.05	0.02
Bi	<b>61.12</b>	59.88–62.63	59.90	60.84	61.23	61.80	62.63	<b>63.06</b>	62.47–64.33	62.52	62.47	63.14	63.15	64.22
Te	<b>37.97</b>	36.88–39.10	39.09	38.83	37.50	37.79	36.88	<b>36.44</b>	35.40–37.22	37.22	36.83	36.24	36.48	35.66
S	<b>0.01</b>	0.00–0.05	0.00	0.05	0.00	0.00	0.00	<b>0.01</b>	0.00–0.11	0.00	0.00	0.11	0.00	0.00
Total	<b>99.50</b>	98.50–100.77	99.45	100.13	99.05	99.89	100.02	<b>99.80</b>	99.66–100.60	99.93	99.66	99.92	99.94	100.07
Pb	<b>0.004</b>		0.007	0.004	0.003	0.004	0.002	<b>0.003</b>		0.000	0.004	0.005	0.004	0.003
Cd	<b>0.004</b>		0.001	0.004	0.004	0.002	0.011	<b>0.003</b>		0.005	0.003	0.004	0.001	0.001
Bi	<b>0.987</b>		0.963	0.971	0.995	0.996	1.011	<b>1.024</b>		1.010	1.014	1.020	1.025	1.046
Te	<b>1.004</b>		1.029	1.015	0.998	0.998	0.975	<b>0.969</b>		0.985	0.979	0.959	0.970	0.951
S	<b>0.001</b>		0.000	0.005	0.000	0.000	0.000	<b>0.001</b>		0.000	0.000	0.012	0.000	0.000
Sum	<b>2.000</b>		2.000	2.000	2.000	2.000	2.000	<b>2.000</b>		2.000	2.000	2.000	2.000	2.000
Bi:Te	<b>0.99</b>	0.94–1.04	0.94	0.96	1.01	1.01	1.04	<b>1.06</b>	1.03–1.10	1.03	1.04	1.06	1.06	1.10

\* mean and range of all measurements, followed by selected representative analyses



**Fig. 3** Plot Te vs. S + Se (at. %) for studied Bi tellurides and sulphotellurides.

$\text{Bi}_{1.02}\text{Te}_{0.97}$  (average of 14 spot analyses, based on 2 *apfu*). Yet, their composition falls within the range 42–50 at. % Te published for tsumoite solid solution in the binary system Bi–Te (Okamoto and Tanner 1990). The observed non-stoichiometry for tsumoite from Libčice probably indicates variation of conditions in the course of crystallization (such as changes in the Bi:Te ratio, temperature and/or pressure – Melnikov et al. 2005).

A X-ray powder diffraction pattern for tsumoite from Libčice was measured, beside the usual Bragg-Brentano setup, also using the Debye-Scherrer's geometry to reduce preferred orientation of the sample, caused by the perfect cleavage of the mineral. Decreasing relative intensity of the *00l* diffraction type maxima (Tab. 2) indicates that the use of Debye-Scherrer's geometry resulted in minimizing the preferred orientation effect. The obtained patterns correspond to theoretical values calculated from the BiTe crystal structure (Yamana et al. 1979) and data reported for natural tsumoite by Shimazaki and Ozawa (1978), Zavjalov et al. (1978) and Gamjanin et al. (1980). Refined unit-cell parameters for tsumoite from Libčice

**Tab. 2** X-ray powder diffraction pattern of tsumoite from Libčice (Å)

			calculated data		Bragg-Brentano		Debye-Scherrer	
<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{calc.}}$	$I_{\text{calc.}}$	$d_{\text{obs.}}$	$I_{\text{obs.}}$	$d_{\text{obs.}}$	$I_{\text{obs.}}$
0	0	1	24.002	4				
0	0	2	12.001	1				
0	0	3	8.001	1				
0	0	5	4.800	4	4.798	28	4.806	15
0	1	1	3.783	4	3.776	2	3.785	14
0	1	3	3.455	1				
1	0	4	3.229	100	3.229	100	3.229	100
1	0	6	2.767	1	2.775	2		
0	1	8	2.362	40	2.364	35	2.365	35
1	1	0	2.212	36	2.211	7	2.212	21
1	0	9	2.189	3	2.189	4	2.189	12
0	1	10	2.034	1				
1	1	5	2.009	1	2.010	11	2.007	9
1	1	-5	2.009	1	2.010	11	2.007	9
0	0	12	2.000	7	2.004	25	2.007	9
2	0	1	1.909	1	1.908	2		
0	2	4	1.825	20	1.825	5	1.825	13
0	1	13	1.663	2	1.665	4	1.666	8
2	0	8	1.614	13	1.615	10	1.615	17
0	2	9	1.556	1	1.556	2	1.557	11
1	1	12	1.4834	9	1.4854	10	1.4851	20
1	1	-12	1.4834	9	1.4854	10	1.4851	20
0	0	17	1.4119	1	1.4142	1	1.4126	3
1	2	-4	1.4074	9	1.4072	2	1.4064	17
2	1	4	1.4074	9	1.4072	2	1.4064	17
1	0	16	1.3968	6	1.4001	11	1.3984	5
2	0	13	1.3292	1	1.3304	2	1.3293	1
2	1	-8	1.3039	6	1.3043	2	1.3042	13
1	2	8	1.3039	6	1.3043	2	1.3042	13
3	0	0	1.2768	6	1.2747	2	1.2749	9

Theoretical data (with  $I_{\text{calc.}} > 0.6$ ) were calculated by program Lazy Pulverix (Yvon et al. 1977) using the crystal structure information on synthetic tsumoite (Yamana et al. 1979)

**Tab. 3** Unit-cell parameters of tsumoite indexed to the trigonal space group P-3m1

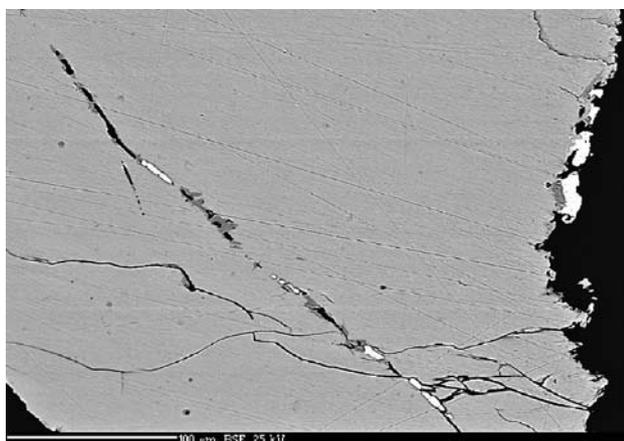
		$a$ [Å]	$c$ [Å]	$V$ [Å <sup>3</sup> ]
Libčice BB*	this paper	4.4210(8)	24.055(6)	407.2(1)
Libčice D	this paper	4.4204(9)	24.043(7)	406.9(1)
synthetic	Yamana et al. (1979)	4.423(2)	24.002(6)	406.6
Tsumo	Shimazaki and Ozawa (1978)	4.422(2)	24.05(2)	407.3
Příbram-Bytíz	Litochleb et al. (2005)	4.423(1)	24.01(1)	406.8(2)
Burčaginkan	Zavjalov et al. (1978)	4.427	24.06	408.4
Tyrnyauz	Zavjalov et al. (1978)	4.425	24.04	407.6
Ilkovcy-Podulky	Zavjalov et al. (1978)	4.421	24.06	407.2
Tyrnyauz	Zavjalov et al. (1978)	4.411	24.18	407.4
Miller-Kopper	Zavjalov et al. (1978)	4.408	24.18	406.9
Alekseevskoje	Zavjalov et al. (1978)	4.408	24.18	406.9

\*BB – Bragg-Brentano, D – Debye-Scherrer geometries

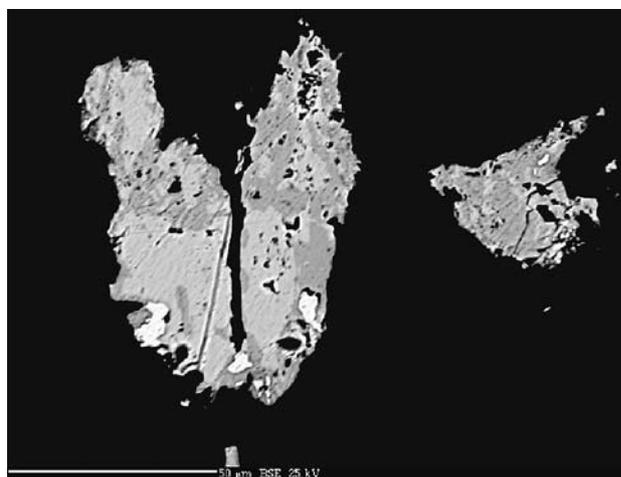
(Tab. 3) compare closely with data published for this mineral. Differences in parameters obtained using the two measurement geometries are in the range of calculated standard deviations.

### 4.3. Tetradyomite

In the studied mineral association tetradyomite is younger than tsumoite and comparatively rare. Typically it forms irregular minute aggregates (1–10 µm), which partly overgrow and replace older tsumoite associated with gold (Fig. 4). Examples of irregular aggregates of tsumoite up to 100 µm, almost completely replaced by tetradyomite and gold, are scarce (Fig. 5). Tetradyomite in intergrowth with Bi–Te phases is distinctly darker grey; it is anisotropic and shows bireflection with grey to grey–brown colour effects. Chemical composition of the



**Fig. 4** Dark irregular aggregates of tetradyomite, which penetrate along fractures, partly overgrow and replace older tsumoite (light grey) associated with gold (white) (BSE image).



**Fig. 5** Irregular tsumoite aggregates (light grey) extensively replaced by younger tetradyomite (dark grey) and gold (white) (BSE image).

studied tetradyomite (Tab. 4) is near the ideal composition of this mineral (Fig. 3). The Sb and Se are not present in detectable abundances, the maximum content of Cd is 0.01 *apfu* and Pb content lower than 0.01 *apfu*. The average Te:S ratio 2.01 (1.90–2.24) is near the theoretical 2:1. The empirical formula of tetradyomite (average of 5 spot analyses) is  $(\text{Bi}_{2.00}\text{Cd}_{0.01})_{\Sigma 2.01}\text{Te}_{2.00}\text{S}_{0.99}$ , based on 5 *apfu*.

### 4.4. Pilsenite

Pilsenite has been observed as a single cleavable aggregate 70 by 80 µm in size, intergrown with gold (Fig. 6) in quartz gangue. It is light grey in reflected light, compared to tsumoite it shows slightly higher reflectivity and under crossed polarizers it is weakly anisotropic (with grey–brown colour effects). Chemical composition of

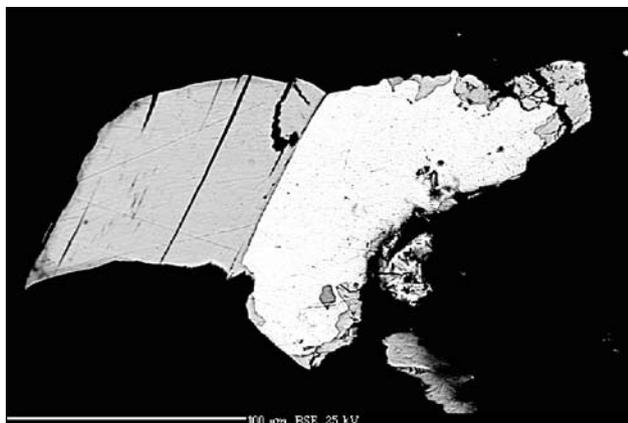
**Tab. 4** Chemical composition of tetradyomite and pilsenite from Libčice (wt. %). Number of atoms based on 5 *apfu* (tetradyomite) and 7 *apfu* (pilsenite)

	tetradyomite						pilsenite					
	mean (n = 5)	1	2	3	4	5	mean (n = 5)	1	2	3	4	5
Pb	<b>0.04</b>	0.08	0.00	0.09	0.00	0.00	<b>0.09</b>	0.08	0.07	0.16	0.06	0.08
Cd	<b>0.11</b>	0.11	0.14	0.17	0.08	0.04	<b>0.12</b>	0.08	0.12	0.16	0.13	0.11
Bi	<b>59.07</b>	59.42	59.17	59.07	59.11	58.58	<b>67.63</b>	67.48	68.18	67.47	67.06	67.98
Te	<b>36.08</b>	36.09	36.82	35.47	35.59	36.41	<b>31.46</b>	31.47	31.36	31.55	31.63	31.31
S	<b>4.50</b>	4.51	4.14	4.69	4.55	4.60	<b>0.00</b>	0.00	0.00	0.00	0.00	0.00
Total	<b>99.78</b>	100.22	100.25	99.48	99.33	99.63	<b>99.30</b>	99.11	99.73	99.33	98.87	99.48
Pb	<b>0.001</b>	0.003	0.000	0.003	0.000	0.000	<b>0.005</b>	0.005	0.004	0.009	0.003	0.005
Cd	<b>0.007</b>	0.007	0.009	0.011	0.005	0.003	<b>0.013</b>	0.008	0.013	0.017	0.014	0.012
Bi	<b>2.000</b>	2.004	2.017	1.994	2.008	1.975	<b>3.963</b>	3.961	3.983	3.949	3.940	3.981
Te	<b>2.000</b>	1.994	2.055	1.961	1.980	2.011	<b>3.019</b>	3.026	3.000	3.024	3.043	3.003
S	<b>0.992</b>	0.992	0.919	1.031	1.007	1.012	<b>0.000</b>	0.000	0.000	0.000	0.000	0.000
Sum	<b>5.000</b>	5.000	5.000	5.000	5.000	5.000	<b>7.000</b>	7.000	7.000	7.000	7.000	7.000

pilsenite (Tab. 4) matches well the theoretical formula  $\text{Bi}_4\text{Te}_3$  (Figs 2–3). Minor Cd corresponds to 0.01 *apfu*, Pb is lower than 0.01 *apfu*; Sb, S and Se were not detected. Its chemical composition (average of 5 spot analyses) yields a theoretical formula  $(\text{Bi}_{3.96}\text{Cd}_{0.01}\text{Pb}_{0.01})_{\Sigma 3.98}\text{Te}_{3.02}$  based on 7 *apfu*.

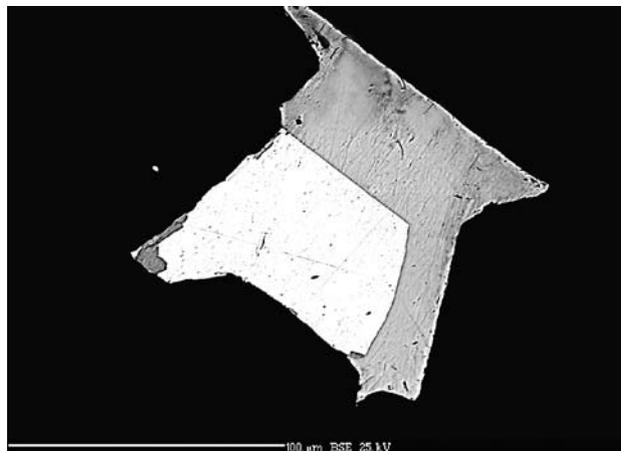
#### 4.5. Other ore minerals

**Gold** forms tiny grains, dendritic aggregates up to 1 mm or occurs as thin coatings on wallrock fractures close to the quartz vein. Microscopic study shows that gold (A) forms subhedral grains up to 100  $\mu\text{m}$ , which are older than the pilsenite (Fig. 6) or tsumoite (Fig. 7). In other places occur small irregular aggregates of younger gold (B), 5–30  $\mu\text{m}$  across, which, together with tetradymite, are associated with earlier tsumoite (Figs 4–5). Gold is deep yellow in reflected light, and optically homogeneous, except for local and small tetradymite inclusions. The older generation of gold (A) with an average composition of Ag = 3.58 (3.25–3.93), Au = 94.69 (93.83–95.63), Hg = 0.72 (0.30–1.08), Cu = 0.14 (0.11–0.17), Bi = 0.05 (0.02–0.10) wt. %, corresponds well to data published previously for older gold generation I from Libčice (Šrein et al. 1995; Zachariáš et al. 1997). Gold in intergrowth with pilsenite contains lower Ag (up to 0.061 *apfu*) and Hg (up to 0.005 *apfu*) than gold in association with tsumoite (Ag up to 0.070, Hg up to 0.010 *apfu*).



**Fig. 6** Gold aggregate (white) overgrown by, and intergrown with, an aggregate of cleavable pilsenite (light grey). Tetradymite forms minute dark inclusions in gold (BSE image).

Hexagonal **pyrrhotite** strongly predominates in the studied mineral association. It forms fine-grained impregnations or irregular aggregates up to 1 cm in recrystallized quartz. Pyrrhotite has a metallic lustre and light beige–brown colour. In reflected light pyrrhotite is pinkish-brown, anhedral to subhedral and it is mostly replaced, except for small relics, by pyrite and



**Fig. 7** Crystal of gold (white) overgrown by tsumoite (light grey) and replaced from the margins by tetradymite (dark grey) (BSE image).

arsenopyrite. Chemical composition is very simple as no additional elements are present in addition to Fe and S (Fe = 59.65–59.75, S = 39.48–40.01, total 99.17–99.66 wt. %). Iron content in pyrrhotite (calculated to 1 *apfu* S) is 0.856–0.867 *apfu*, which for the empirical formula  $\text{Fe}_{1-x}\text{S}$  yields value  $x = 0.13\text{--}0.14$ . Such a composition falls in the range for natural pyrrhotites, for which  $x = 0\text{--}0.17$  was reported (Anthony et al. 1990). No indications of transformation of pyrrhotite to marcasite have been observed either in reflected light or in BSE images. On the other hand, the alteration of pyrrhotite to marcasite is a characteristic feature of the younger (post-metamorphic) stages of mineralization in the studied vein (Šrein et al. 1995).

## 5. Conditions of formation

The studied mineralization with macroscopic Bi–Te minerals and gold of high fineness belongs to Au–quartz mineralization, which is widespread throughout the Central Bohemian Metallogenic Zone (Morávek et al. 1992). Compared to similar deposits and occurrences in this zone (e.g. Jílové near Prague, Nový Knín, Mokrsko–Čelina), the studied locality differs by the presence of younger contact metamorphic phenomena, which affected the mineralogical composition, structure of the gangue and character of the ore mineralization.

The observed crystallization sequence: gold A  $\rightarrow$  tsumoite (+ pilsenite)  $\rightarrow$  tetradymite  $\rightarrow$  gold B and relative abundance of individual minerals permit to define at least two stages of crystallization in this mineral association. The more important first stage, which was responsible for deposition of pyrrhotite, gold A, tsumoite (both varieties) and pilsenite (all phases with ratio  $\text{Me}/(\text{Te} + \text{Se} + \text{S}) \geq 1$ ) was characterized by high activity of bismuth at low

values of  $f_{S_2}$  (S-free Bi tellurides, presence of pyrrhotite) and locally variable but relatively high values  $f_{Te_2}$  in hydrothermal fluids (Afifi et al. 1988; Cook and Ciobanu 2004 among others). The non-stoichiometry of the later tsumoite generation, the presence of its two chemically distinct varieties and the absence of native bismuth in the assemblage may indicate formation at elevated temperatures (>300 °C) and somewhat variable conditions (e.g., changing Bi:Te ratio, temperature and/or pressure). Based on study of fluid inclusions from Libčice by Zachariáš et al. (1997), the following formation conditions were estimated for quartz and gold of the older generation:  $T = 290$  to  $310$  °C and  $P = 1.2$ – $1.6$  kbar. Formation of the abundant older pyrrhotite probably resulted from metamorphic recrystallization of the original pyrite. The second stage, products of which are subordinate, is characterized by a replacement of the older Bi–Te minerals by tetradymite, gold B, and by an origin of pyrrhotite of younger generation, pyrite and arsenopyrite. This development indicates a notable decline in Bi activity and an increase in  $f_{S_2}$  in hydrothermal fluids (Affifi et al. 1988). A straightforward interpretation of minerogenesis at the Libčice deposit is significantly complicated by variable manifestations of hydrothermal and, especially, metamorphic processes in space and time. The two stages probably can represent a “primary” hydrothermal episode and a younger contact metamorphic (recrystallization) overprinting event.

## 6. Conclusions

A mineral association consisting of dominant pyrrhotite, tsumoite and gold, with accessory tetradymite and pilsenite, has been identified in high-grade gold ore from the main vein of the Libčice deposit. Study of chemical composition of tsumoite resulted in identification of its stoichiometric (predominating matrix) and a Bi-rich (in the form of schlieren) varieties. The compositional range of tsumoite from Libčice corresponds to data published for this mineral. Coexisting tetradymite and pilsenite are close to ideal stoichiometry, pyrrhotite is characterized by the formula  $Fe_{1-x}S$  with  $x$  values in the range 0.13–0.14; gold contains low Ag (up to 4 wt. %) and Hg (up to 1 wt. %) admixtures.

The studied mineral association formed at elevated temperatures (>300 °C), probably in two stages with declining activities of bismuth and variable  $f_{S_2}$  and  $f_{Te_2}$ . The origin of tetradymite after tsumoite and the replacement of older pyrrhotite by pyrite with arsenopyrite indicate a sulphidation of the assemblage in the second stage. The two stages probably represent a “primary” hydrothermal episode and a younger contact metamorphic (recrystallization) overprinting event.

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