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PŮVODNÍ PRÁCE/ORIGINAL PAPER

Enargite, tennantite-(Cu) and tangdanite from the Gápeľ copper deposit near Dobšiná, Spišsko-gemerské rudohorie Mts., Slovakia

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Abstract

A new occurrence of enargite, tennantite-(Cu) and tangdanite was recently discovered at the Gápeľ copper deposit near Dobšiná, Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Slovakia. Enargite is rare mineral at the studied locality and it occurs as dark-grey, metallic, prismatic crystals up to 2.5 mm with perfect cleavage, developed on fractures of quartz-dolomite gangue. Its refined unit-cell parameters (for the orthorhombic space group *Pmn*2₁) are: *a* 7.4031(7) Å, *b* 6.4321(6) Å, *c* 6.1466(7) Å and *V* 292.68(4) Å³. Its chemical composition corresponds to empirical formula Cu_{3.04}As_{0.98}S_{3.98}. Tennantite-(Cu) forms anhedral grains and aggregates replacing crystals of enargite. Its empirical formula is Cu_{6.00}[Cu_{4.00}(Cu_{1.07}Fe_{0.64}Zn_{0.42})_{Σ2.13}]As_{3.87}S_{13.04}. Tangdanite occurs as turquoise-blue to blue-green radial aggregates up to 3 mm with silky lustre, developed on fractures of quartz gangue with partly weathered aggregates of minerals of the tennantite series. Its chemical composition corresponds to empirical formula Ca_{2.12}(Cu_{8.77}Zn_{0.19})_{Σ8.96}[(AsO₄)_{3.91}(PO₄)_{0.08}(SiO₄)_{0.01}]_{Σ4.00}(SO₄)_{0.43}(OH)_{9.30}·9H₂O.

Key words: enargite, tennantite-(Cu), tangdanite, chemical composition, siderite veins, Gápeľ copper deposit, Dobšiná, Gemeric Unit, Spišsko-gemerské rudohorie Mts., Slovak Republic

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Introduction

The Spišsko-gemerské rudohorie Mts. represents one of the most important accumulations of ore deposits in the Carpathians. 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 and sulfosalts (extensively exploited especially for iron and copper as well as minor amounts of mercury, silver, nickel and cobalt in Dobšiná, Štítnik, Rákoš, Rožňava, Drnava, Rudňany, Novoveská Huta, Hnilčík, Henclová, Gelnica, Slovinky, Medzev etc.) and quartz-stibnite veins (e.g. Betliar, Čučma, Bystrý potok, Štofova dolina, Helcmanovce, Poproč or Zlatá Idka) (Varček 1962; Chovan et al. 1994; Grecula et al. 1995).

The Gápeľ copper deposit (also known as Schwarzenberg or Gápeľ vein system) was in the Medieval times one of the most important sources of the copper ores in the area of Dobšiná (Rozložník 1935; Grecula et al. 1995). Nevertheless, there are only very limited data available about the mineralogy of this interesting system of hydrothermal quartz-carbonate veins with sulfides (e.g. unpublished reports of Halačková-Andrusovová 1959; Háber 1978a). Based on geochemical and geological features, the Gápeľ copper deposit is considered as western continuation of the Novoveská Huta-Hanisková vein system (Háber 1978a; Grecula et al. 1995), where besides of dominant chalcopyrite minerals of the tennantite-tetra-

hedrite series as well as accessory enargite are typical ore minerals (Háber 1978b, 1985; Háber et al. 1993).

Enargite, tennantite-(Cu) and tangdanite were recently identified at the Gápeľ copper deposit in ore samples collected in October-November 2022 by Marek Szabó Dózsa. Their mineralogical description is presented in this paper.

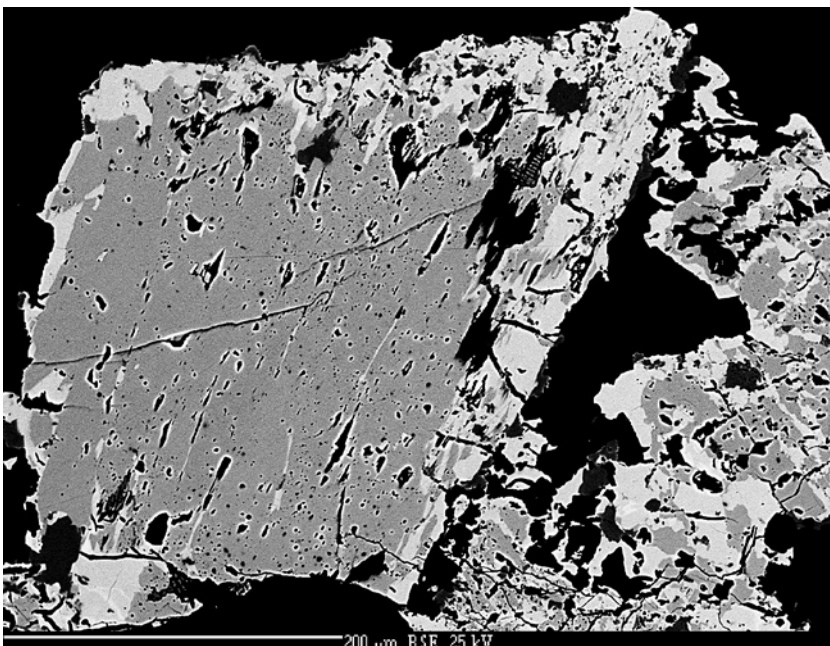
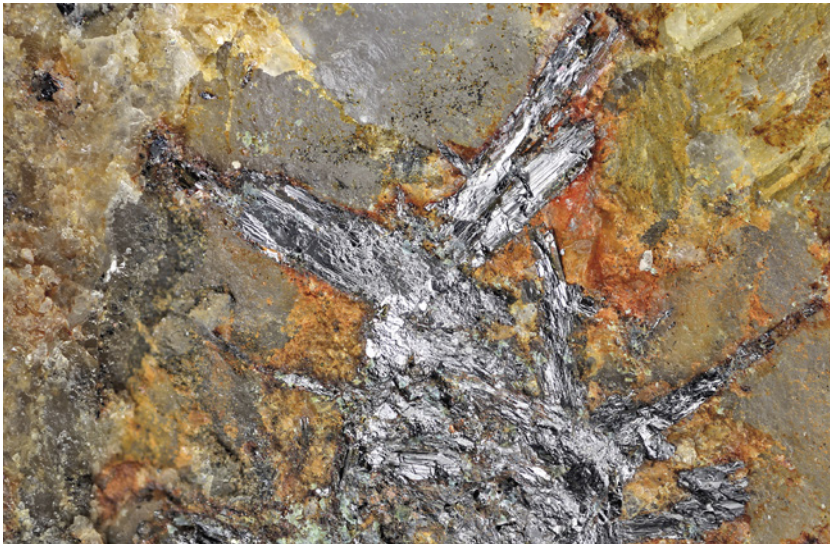
Geological setting

The Gápeľ copper deposit is situated around 3.8 km NNW of the Dobšiná town, 400 m NW of the Gápeľ hill (961 m a.s.l.) in the Spišsko-gemerské rudohorie Mts., Rožňava Co., Košice Region, Slovakia. Ore samples with enargite, tennantite-(Cu) and tangdanite were collected at the dump of the Horný Viliam adit (Fig. 1). GPS coordinates (WGS84) of this dump are: 48.847837° N and 20.339154° E, 878 m a.s.l.

The system of hydrothermal quartz-carbonate veins with ore mineralization at the Gápeľ deposit is hosted in the Permian sandstones of the Knola Formation representing the base of the Krompachy Group (Novotný, Mihál 1987; Vozárová 1996). The Gápeľ deposit consists of mostly NW - SE trending, up to 3 m thick ore veins. The tree main veins are known: Kyzová (Kiesgang), Chudobná (Armer Gang) and Bohatá (Reicher Gang) and the average ore was containing up to 2 % of Cu (Rozložník 1935). The dominant gangue minerals are quartz



Fig. 1 Dump of the Horný Viliam adit at the Gápel' copper deposit near Dobšiná. Photo by M. Szabó Dózsa, October 2022.



and minerals of the dolomite-ankerite series, accompanied by minor tourmaline and abundant sulfides, represented mainly by chalcopyrite and pyrite and minor amounts of minerals of the tetrahedrite group and arsenopyrite (Halahyová-Andrusovová 1959). Háber (1978a) also briefly mentioned occurrence of siderite, calcite, gypsum/baryte, hematite, marcasite, enargite, sphalerite, galena and rutile, but without any further details or analytical data.

Analytical methods

Powder X-ray diffraction data of enargite were collected on a Bruker D8 Advance diffractometer (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic) with a solid-state 1D Lynx-Eye detector using $\text{CuK}\alpha$ radiation and operating at 40 kV and 40 mA. The powder pattern was collected using Bragg-Brentano geometry in the range $5 - 70^\circ 2\theta$, 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 enargite (Karanović et al. 2002), based on Lazy Pulverix program (Yvon et al. 1977).

The quantitative (WDS) chemical analyses of enargite, tennantite-(Cu) and tanguanite were performed using a Cameca SX100 electron microprobe (Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic). The following conditions, standards and X-ray lines were used: *for enargite and tennantite-(Cu)*: 25 kV, 20 nA,

Fig. 2 Prismatic crystals of enargite from the Gápel' copper deposit near Dobšiná. Field of view is 5.07 mm. Photo by L. Hrdlovič.

Fig. 3 Enargite (dark grey) replaced by slightly zonal tennantite-(Cu) (light grey). BSE image by J. Sejkora.

0.7 μm wide beam, 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(Br,I) (TlL α), and ZnS (ZnK α); for *tangdanite*: 15 kV, 5 nA and 5 μm wide beam, albite (NaK α), apatite (CaK α , PK α), baryte (BaL α), Bi (BiM α), celestine (SrL β , SK α), clinoclase (AsL α), Co (CoK α), CuFeS₂ (CuK α), diopside (MgK α), halite (ClK α), hematite (FeK α), LIF (FK α), Ni (NiK α), rhodonite (MnK α), sanidine (AlK α , KK α , SiK α), Sb₂S₃ (SbL α), vanadinite (PbM α , VK α) and ZnO (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).

Results

Enargite is rare mineral at the studied locality. It forms dark-grey, metallic, prismatic crystals up to 2.5 mm long with perfect cleavage (Fig. 2), developed on fractures of quartz-dolomite gangue. Crystals and aggregates of enargite are replaced (Fig. 3) by tennantite-(Cu) to tennantite-(Fe).

The experimental X-ray powder pattern of enargite from the Gápel deposit (Table 1) agree very well with published data for enargite as well as with those calculated from the crystal structure of this mineral published by Karanović et al. (2002). Some observed differences in intensities of individual diffraction maxima are caused by preferred orientation effects. The refined unit-cell parameters of studied enargite, compared with published data, are given in the Table 2.

Quantitative WDS chemical analyses of enargite from the Gápel copper deposit and the corresponding empirical formulae are shown in Table 3. Studied enargite is compositionally close to the ideal end member with average ($n = 15$) empirical formula (based on sum of all atoms = 8 *apfu*) expressed as Cu_{3.04}As_{0.98}S_{3.98}.

Tennantite-(Cu) occurs as anhedral grains and aggregates replacing crystals of enargite (Fig. 3). It shows slight chemical zoning which is caused by variation of Cu, Fe and Zn contents (Table 4, Fig. 4). Its chemical composition corresponds to recently defined tennantite-(Cu), copper dominant member of tennantite series (Biagioni et al. 2022). Its average ($n = 14$) empirical formula based on sum of Me = 16 *apfu* is Cu_{6.00}[Cu_{4.00}(Cu_{1.07}Fe_{0.64}Zn_{0.42})_{2.13}]As_{3.87}S_{13.04}.

Tangdanite is rare mineral at the studied locality. It forms turquoise-blue to blue-green radial aggregates up to 3 mm with silky lustre (Fig. 5), developed on fractu-

Table 1 X-ray powder diffraction data of enargite from the Gápel copper deposit

d_{obs}	I_{obs}	d_{calc}	h	k	l	d_{obs}	I_{obs}	d_{calc}	h	k	l	d_{obs}	I_{obs}	d_{calc}	h	k	l
4.859	3.6	4.855	1	1	0	2.2198	20.4	2.2193	2	1	2	1.5884	16.0	1.5883	2	3	2
3.216	67.4	3.216	0	2	0	1.8552	71.0	1.8553	2	3	0	1.5855	4.0	1.5855	4	0	2
3.208	100.0	3.208	2	1	0	1.8506	41.5	1.8508	4	0	0	1.5554	3.3	1.5557	0	4	1
3.074	45.1	3.073	0	0	2	1.7276	35.7	1.7280	0	2	3	1.5522	3.8	1.5521	4	2	1
2.849	29.8	2.850	0	2	1			1.7268	2	1	3	1.5362	2.0	1.5366	0	0	4
2.844	58.0	2.844	2	1	1	1.6083	4.1	1.6080	0	4	0	1.4221	3.4	1.4221	4	2	2
2.2223	5.2	2.2219	0	2	2	1.6039	7.0	1.6041	4	2	0						

Table 2 Unit-cell parameters of enargite from the Gápel copper deposit (for orthorhombic space group *Pmn2*₁) compared with published data

		a [Å]	b [Å]	c [Å]	V [Å ³]
Gápel	this paper	7.4031(7)	6.4321(6)	6.1466(7)	292.68(4)
Bor, Serbia	Karanović et al. (2002)	7.4127(16)	6.4404(15)	6.1577(14)	293.97
Butte, USA	Adiwidjaja, Lohn (1970)	7.407(1)	6.436(1)	6.154(1)	293.37
synth.	Pfzner, Bernert (2004)	7.399(1)	6.428(1)	6.145(1)	292.3(1)
Bailadores	Henao et al. (1994)	7.426(1)	6.4521(9)	6.1631(9)	295.3(1)

Table 3 Quantitative WDS analyses of enargite from the Gápel copper deposit (wt.%)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Cu	49.57	49.40	49.40	49.51	49.52	49.45	49.69	49.36	49.82	49.78	49.64	49.63	49.86	49.38	49.42
As	19.050	18.970	18.940	19.010	18.910	19.070	18.930	19.210	18.390	18.280	18.370	19.170	18.970	18.770	18.720
S	32.600	32.440	32.540	32.410	32.380	32.650	32.580	32.370	33.260	33.250	33.240	32.540	32.690	32.760	32.860
total	101.22	100.81	100.88	100.93	100.81	101.17	101.20	100.94	101.47	101.31	101.25	101.34	101.52	100.91	101.00
Cu	3.043	3.045	3.041	3.050	3.054	3.035	3.051	3.042	3.035	3.036	3.029	3.045	3.051	3.034	3.032
As	0.992	0.992	0.989	0.993	0.989	0.993	0.986	1.004	0.950	0.946	0.951	0.998	0.985	0.978	0.974
S	3.966	3.963	3.970	3.957	3.957	3.972	3.964	3.954	4.015	4.019	4.020	3.957	3.964	3.988	3.995

calculated empirical formulae are based on sum of all atoms = 8 *apfu*

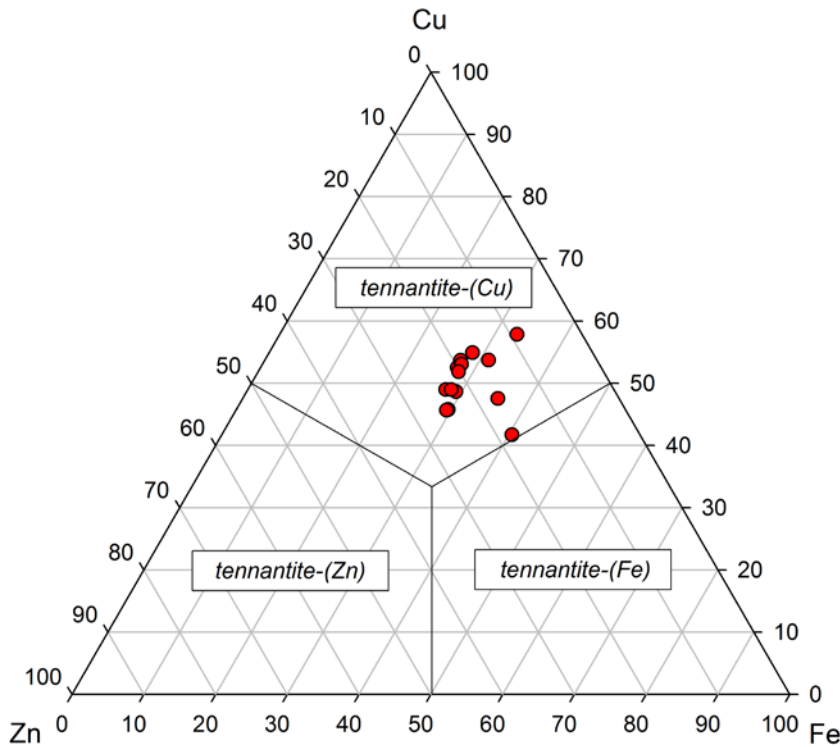


Fig. 4 Ternary diagram of divalent metals Cu*-Zn-Fe in C position (at. %; Cu* = total Cu-10) for tennantite-(Cu) from the Gápel' copper deposit near Dobšiná.

Table 4 Quantitative WDS analyses of tennantite-(Cu) from the Gápel' copper deposit (wt.%)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cu	48.55	48.74	48.64	48.63	48.48	48.19	48.22	48.01	48.20	49.10	48.77	47.80	48.05	47.76
Fe	2.21	2.22	2.30	2.33	2.35	2.50	2.31	2.30	2.92	2.62	2.49	2.39	2.40	3.20
Zn	1.89	1.81	1.59	1.89	1.99	2.22	2.30	2.15	1.62	0.84	1.41	2.34	2.39	1.65
As	20.14	20.06	19.94	19.54	19.51	19.25	19.57	19.89	19.95	20.42	20.34	19.98	20.02	20.52
S	28.62	28.77	28.62	28.93	29.04	29.12	28.89	29.06	28.51	28.56	28.39	28.76	28.70	28.43
total	101.41	101.60	101.09	101.32	101.37	101.28	101.29	101.41	101.20	101.54	101.40	101.27	101.56	101.56
Cu A+B sites	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000
Cu C site	1.100	1.134	1.163	1.165	1.139	1.091	1.072	1.039	1.014	1.188	1.112	0.966	0.970	0.853
Fe	0.575	0.577	0.601	0.609	0.614	0.655	0.604	0.602	0.759	0.679	0.646	0.624	0.623	0.827
Zn	0.420	0.402	0.355	0.422	0.444	0.497	0.513	0.480	0.360	0.186	0.312	0.522	0.530	0.364
Σ C site	2.095	2.113	2.118	2.195	2.198	2.242	2.189	2.121	2.133	2.054	2.069	2.112	2.123	2.045
As	3.905	3.887	3.882	3.805	3.802	3.758	3.811	3.879	3.867	3.946	3.931	3.888	3.877	3.955
S	12.967	13.025	13.017	13.162	13.223	13.282	13.146	13.241	12.911	12.897	12.818	13.076	12.985	12.803

calculated empirical formulae are based on sum of Me = 16 apfu



Fig. 5 Radial aggregates of tennantite from the Gápel' copper deposit near Dobšiná. Field of view is 5.32 mm. Photo by L. Hrdlovič.

Table 5 Quantitative WDS analyses of tangdanite from the Gápel copper deposit (wt.%)

	1	2	3	4	5	6	7	8	9	10	11	12	13
CaO	7.71	7.63	7.46	7.91	7.88	7.86	7.91	7.80	7.95	7.77	7.32	7.66	7.62
CuO	45.04	46.08	44.93	44.89	45.03	45.61	45.11	45.54	45.11	44.98	45.12	45.43	45.05
ZnO	1.18	1.13	1.12	0.82	1.13	0.99	0.85	0.81	0.88	0.90	1.12	0.94	1.15
Al ₂ O ₃	0.05	0.00	0.00	0.04	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.00
As ₂ O ₅	28.75	29.30	29.46	28.94	29.12	29.36	29.11	29.61	29.36	29.54	28.79	28.88	28.92
P ₂ O ₅	0.31	0.34	0.34	0.28	0.33	0.32	0.31	0.32	0.35	0.38	0.40	0.40	0.38
SO ₃	2.25	2.43	2.33	2.12	2.24	2.29	2.10	2.17	2.37	2.32	2.12	1.97	2.28
H ₂ O*	15.90	16.10	15.85	15.89	15.99	16.07	15.95	16.05	15.95	15.91	15.80	16.01	15.86
total	101.19	103.01	101.82	100.89	101.78	102.50	101.34	102.30	101.97	101.80	100.67	101.61	101.26
Ca	2.160	2.095	1.996	2.206	2.178	2.156	2.190	2.122	2.178	2.112	2.038	2.083	2.115
Cu	8.898	8.921	8.474	8.826	8.775	8.822	8.803	8.735	8.711	8.620	8.857	8.711	8.814
Zn	0.228	0.214	0.206	0.158	0.215	0.187	0.162	0.152	0.166	0.169	0.215	0.176	0.220
Al	0.015	0.000	0.000	0.012	0.018	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Σ B cations	9.141	9.135	8.680	8.995	9.009	9.009	8.965	8.887	8.877	8.788	9.072	8.887	9.034
Si	0.000	0.000	0.082	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.081	0.000
As	3.931	3.926	3.846	3.938	3.928	3.931	3.932	3.931	3.924	3.918	3.912	3.833	3.917
P	0.069	0.074	0.072	0.062	0.072	0.069	0.068	0.069	0.076	0.082	0.088	0.086	0.083
Σ Si+As+P	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
S	0.442	0.467	0.437	0.414	0.434	0.440	0.407	0.414	0.455	0.442	0.413	0.375	0.443
OH*	9.735	9.525	8.396	9.587	9.525	9.450	9.496	9.191	9.199	8.917	9.394	9.108	9.412
H ₂ O	9	9	9	9	9	9	9	9	9	9	9	9	9

calculated empirical formulae are based on sum of (Si+As+P) = 4 *apfu*, H₂O* - water content calculation is based on 9 molecules of H₂O in the ideal formula, OH* - content of OH⁻ groups is based on the charge balance

res of quartz gangue with partly weathered aggregates of minerals of the tennantite series. Except of dominant contents of Ca and Cu (Table 5), studied tangdanite from the Gápel copper deposit shows also elevated concentrations of Zn (ranging from 0.15 to 0.23 *apfu*) as well as minor amounts of Al (up to 0.02 *apfu*). Arsenate anion is substituted by minor amounts of P (up to 0.09 *apfu*) and Si (up to 0.08 *apfu*) and sulfur contents are ranging between 0.38 and 0.47 *apfu*. The average (n = 13) empirical formula of tangdanite from the Gápel copper deposit based on sum of (Si+As+P)=4 *apfu* is Ca_{2.12}(Cu_{8.77}Zn_{0.19})_{Σ8.96}[(AsO₄)_{3.91}(PO₄)_{0.08}(SiO₄)_{0.01}]_{Σ4.00}(SO₄)_{0.43}(OH)_{9.30}·9H₂O.

Conclusions

A new occurrence of enargite, tennantite-(Cu) and tangdanite was discovered at the Gápel copper deposit near Dobšiná, Spišsko-gemerské rudohorie Mts., Slovakia. Studied tangdanite was formed by the *in-situ* weathering of minerals of the tennantite series, which were the source of Cu, Zn, As and S. Calcium was most probably liberated from the gangue carbonates (dolomite, calcite) or host rocks by the acidic solutions produced by the weathering of primary ore minerals.

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