

Table 2. Selected electron microprobe analyses of tetrahedrite grains form locality Špania Dolina Piesky and tennantite grains form locality Ľubietová Svätodušná (8 representative analyses for each locality).

Špania Dolina-Piesky										Ľubietová-Svätodušná									
wt%	Cu	Ag	Fe	Zn	As	Sb	Bi	S	Total	wt%	Cu	Ag	Fe	Zn	As	Sb	Bi	S	Total
1	42.37	0.12	3.95	1.23	6.11	20.22	0.68	26.5	101.18	1	40.17	2.03	6.79	0.67	14.52	7.07	1.01	26.94	99.2
2	42.16	0.12	3.81	1.27	5.32	21.41	0.65	26.2	100.95	2	41.74	0.99	6.88	0.63	14.56	7.1	1.04	27.21	100.15
3	41.59	0.13	3.87	1.27	5.04	21.79	0.75	26.21	100.65	3	40.56	1.86	6.81	0.64	14.56	7.04	0.94	26.85	99.27
4	42.45	0.11	3.92	1.18	6.38	20.05	0.75	26.42	101.25	4	41.44	1.23	6.91	0.66	13.86	8.07	1.14	27.13	100.44
5	41.34	0.14	3.87	1.22	5.97	20.23	0.63	26.33	99.73	5	42.52	0.51	6.86	0.61	14.37	7.26	0.88	27.28	100.29
6	41.97	0.14	3.79	1.21	4.53	22.01	0.82	26.09	100.56	6	42.35	0.67	6.91	0.59	14.32	7.37	0.91	27.27	100.4
7	42.24	0.13	3.87	1.16	5.68	20.14	0.55	26.32	100.09	7	42.24	0.6	6.85	0.67	14.85	7.44	0.89	27.05	100.59
8	42.18	0.13	3.86	1.19	5.45	20.58	0.82	26.07	100.28	8	41.78	0.81	6.77	0.62	14.95	7.19	0.87	26.82	99.81
apfu										apfu									
1	10.54	0.02	1.11	0.29	1.28	2.62	0.05	13.06		1	9.75	0.29	1.88	0.16	2.99	0.9	0.07	12.96	
2	10.57	0.02	1.09	0.31	1.13	2.8	0.05	13.02		2	10	0.14	1.88	0.15	2.96	0.89	0.08	12.92	
3	10.48	0.02	1.11	0.29	1.08	2.87	0.06	13.09		3	9.84	0.27	1.88	0.15	3.00	0.89	0.07	12.91	
4	10.56	0.02	1.11	0.28	1.35	2.6	0.06	13.02		4	9.95	0.17	1.89	0.15	2.82	1.01	0.08	12.91	
5	10.42	0.02	1.11	0.3	1.28	2.66	0.05	13.16		5	10.15	0.07	1.86	0.14	2.91	0.9	0.06	12.9	
6	10.6	0.02	1.09	0.3	0.97	2.90	0.06	13.06		6	10.11	0.09	1.88	0.14	2.9	0.92	0.07	12.9	
7	10.61	0.02	1.11	0.28	1.21	2.64	0.04	13.1		7	10.09	0.08	1.86	0.16	3.01	0.93	0.06	12.81	
8	10.63	0.02	1.11	0.29	1.16	2.71	0.06	13.02		8	10.06	0.12	1.86	0.14	3.05	0.9	0.06	12.8	

Table 3. Representative electron microprobe analyses of X-ray amorphous phases associated with tetrahedrite weathering (b.d.=below the detection limit).

	As₂O₅	CuO	Fe₂O₃	Sb₂O₅	Bi₂O₃	Ag₂O	HgO	PbO	SO₃	Total
1	27.59	27.89	13.77	3.55	4.71	0.01	0.03	0.02	0.04	77.61
2	27.65	28.92	12.82	3.44	2.02	0.01	b.d.	b.d.	0.05	74.91
3	28.86	30.69	13.93	3.74	3.67	0.01	0.02	0.05	0.05	81.02
4	26.75	27.86	14.31	3.67	3.05	0.04	0.01	0.04	0.07	75.8
5	29.34	32.11	14.31	4.20	2.98	0.01	b.d.	b.d.	0.06	83.01
6	25.70	18.67	12.8	3.30	1.92	0.02	0.07	0.02	0.04	62.54
7	26.57	22.02	13.01	3.26	2.29	0.01	b.d.	b.d.	0.06	67.22
8	26.23	30.22	12.78	3.77	2.50	b.d.	b.d.	0.05	0.01	75.56
9	27.12	31.52	14.4	3.74	3.51	0.04	0.12	0.05	0.02	80.52
10	30.93	31.61	14.55	4.63	3.58	0.01	0.09	0.01	0.09	85.5

Table 4. Selected electron microprobe analyses and refined a unit cell parameter (synchrotron μ XRD)- for roméite, possibly in a mixture with the X-ray amorphous phases.

	As ₂ O ₅	CuO	Fe ₂ O ₃	Sb ₂ O ₅	Bi ₂ O ₃	Ag ₂ O	HgO	PbO	CdO	ZnO	SeO ₂	SO ₃	Total	a (Å)
1	24.55	33.74	14.08	18.22	4.31	0.19	0.01	0.05	0.07	0.03	0.24	0.14	95.63	10.331(9)
2	21.49	29.81	11.99	27.26	4.66	0.10	0.00	0.00	0.08	0.08	b.d.	0.09	95.56	10.327(9)
3	25.13	33.21	14.84	19.64	3.12	0.05	0.05	b.d.	b.d.	0.06	b.d.	0.06	96.16	10.357(9)
4	17.24	27.89	11.47	31.84	4.18	0.14	0.08	0.07	0.05	0.04	b.d.	0.10	93.10	10.35(2)
5	22.03	31.69	12.01	26.18	3.86	0.13	0.00	0.05	0.12	0.02	b.d.	0.08	96.17	10.322(4)
6	23.89	31.99	13.61	17.92	3.62	0.21	0.05	0.01	0.08	0.04	0.11	0.16	91.69	10.35(1)
7	24.38	34.68	13.16	21.29	2.14	0.03	0.14	0.09	0.04	0.06	b.d.	0.08	96.09	10.35(1)
8	23.73	31.79	16.39	20.49	2.56	0.01	0.04	0.07	b.d.	0.06	b.d.	0.09	95.23	10.31(1)
9	15.62	40.75	10.51	20.54	0.98	1.57	0.28	0.02	0.01	0.02	0.24	0.57	91.11	10.28(1)

Table 5. Chemical composition of tripuhyite and roméite mixture (wt%) and refined unit cell parameters (synchrotron μ XRD) for the two minerals. * The mass balance calculation: Roméite formula was calculated from EMPA analyses for single roméite phase based on 7 oxygens; in the mixture of tripuhyite and roméite all As and Cu are assumed to be hosted by roméite.

	As ₂ O ₅	CuO	Fe ₂ O ₃	Sb ₂ O ₅	Bi ₂ O ₃	Ag ₂ O	HgO	PbO	CdO	ZnO	SeO ₂	SO ₃	Total	Tripuhyite		Roméite	Mass balance	
														a/ Å	c/ Å	a/ Å	Tripuhyite %	Roméite %
1	6.96	9.99	15.00	54.34	2.64	b.d.	b.d.	0.01	0.05	0.07	b.d.	0.12	89.18	4.56(1)	3.13(2)	10.235(8)	43	57
2	6.94	9.85	16.13	52.74	0.21	0.01	0.08	0.00	0.11	0.06	b.d.	0.03	86.16	4.671(3)	3.036(3)	10.261(4)	44	56
3	7.36	10.15	17.90	51.09	1.07	b.d.	0.02	0.14	0.02	0.05	0.24	0.03	88.07	4.611(8)	3.087(9)	10.28(1)	43	57
4	6.48	10.21	15.91	53.05	b.d.	0.03	0.05	b.d.	0.07	0.04	0.14	0.10	86.08	4.591(8)	3.09(1)	10.266(8)	43	57
5	5.65	8.88	14.37	55.82	1.57	0.04	0.03	0.02	0.13	0.07	b.d.	0.05	86.63	4.586(9)	3.16(1)	10.33(1)	48	52
6	8.06	11.39	18.43	50.65	1.54	0.04	b.d.	0.03	b.d.	0.04	0.05	0.13	90.36	4.59(1)	3.09(2)	10.267(8)	40	60
7	6.60	9.57	14.38	55.48	0.54	0.01	0.03	b.d.	b.d.	0.05	0.25	0.03	86.94	4.55(2)	3.13(2)	10.269(8)	45	55
8	6.07	9.30	13.74	55.97	0.41	0.04	0.02	b.d.	0.07	0.06	0.17	b.d.	85.85	4.573(9)	3.19(1)	10.308(5)	46	54
9	10.34	14.46	24.18	42.77	0.89	0.01	0.01	0.04	0.05	0.08	0.06	0.06	92.95	4.586(2)	3.049(3)	10.201(5)	32	68

Table 6. Results of the LC fits of Sb XANES spectra for the tripuhyite-roméite mixtures resulting from tetrahedrite weathering (analyses 1-6) together with statistical evaluation of goodness of fits. Sum of the components was normalized to 100%.

Analysis	Tripuhyite (Sb ⁵⁺ - O) %	Sb ₂ O ₃ (Sb ³⁺ - O)%	R-factor	Chi-square
1	84	16	0.028272	0.00533
2	88	12	0.004928	0.0009
3	90	10	0.005666	0.00102
4	88	12	0.004495	0.00082
5	100	0	0.053702	0.00922
6	79	21	0.040014	0.0063

Table 7. Chemical composition of X-ray amorphous oxidation products associated with tennantite relics (wt%).

	As₂O₅	SiO₂	Fe₂O₃	ZnO	Bi₂O₃	CuO	SO₃	Sb₂O₅	MgO	CaO	Ag₂O	Total
1	31.04	0.24	14.91	0.06	2.14	34.28	0.36	5.69	0.02	0.13	0.06	88.93
2	31.01	0.27	16.28	0.06	2.15	32.66	0.45	5.74	0.03	0.15	0.03	88.83
3	27.68	0.27	15.16	0.09	1.94	33.69	0.42	5.54	0.03	0.15	0.09	85.06
4	27.74	0.27	12.11	0.09	1.67	39.96	0.55	6.13	0.00	0.07	0.06	88.65
5	29.86	0.25	13.29	0.13	2.06	36.95	0.49	5.86	0.01	0.07	0.00	88.97
6	26.17	0.35	12.26	0.16	1.54	42.97	1.27	6.33	0.03	0.16	0.02	91.26
7	30.41	0.08	14.09	0.07	1.56	35.73	1.90	1.09	0.00	0.15	4.79	89.87
8	30.35	0.17	16.75	0.08	1.97	34.29	0.61	4.69	0.00	0.11	0.03	89.05