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Trends in chemical composition of tetrahedrite from the deposit Jedľovec (Fichtenhübel), Spišsko-gemerské rudohorie Mts.

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Abstract. The deposit Jedľovec with veins Konštancia, Krištof and Michal, located in the central part of the Spišsko-Gemerské Rudohorie Mts., hosts hydrothermal siderite-sulphide mineralisation. Studied samples of tetrahedrite come from veins Konštancia and Krištof. Analyses determined Sb-end member of tetrahedrite with 100 to 83.67 % of tetrahedrite component with substantial Fe content (3.69-6.01 wt.%). Minor elements reach the following maximum values: Ag-1.47, Zn-2.69, Hg-0.51, Bi-0.65 wt.%. According to the chemical composition and textural relations tetrahedrite aggregates were divided into two generations. The older one contains two types of phases typical by Cu-As and Ag-Sb contents. The younger generation is typical by the presence of Hg and Bi, S deficiency and higher concentrations of Cu, PMe and Me^{+2} compared to the older one. Phases of selected generations form a geochemical zoning. Phases of the older generation with typical Cu-As contents are located in the central and lower parts of veins (Konštancia). Phases of older generation, typical by Ag-Sb contents, are present at outskirts and in upper parts of veins (Konštancia, Krištof). Aggregates of the younger generation are located in the narrow, central part of veins (Konštancia).

Keywords: Spišsko-gemerské rudohorie Mts., hydrothermal mineralisation, Fe-tetrahedrite, geochemistry, zoning.

Introduction

Sulphosalts of the tetrahedrite-tennantite series are common minerals at deposits of siderite-sulphide formation of Spišsko-gemerské rudohorie Mts., including the deposit Jedľovec. Bernard (1958) and in particular Trdlička (1967) studied this mineral from the deposit in more details.

Tetrahedrite is a common mineral at the deposit. It forms steel-grey irregular aggregates, penetrating together with chalcopyrite into siderite and quartz in the form of veinlets or a network. It also occurs in the form of small lenses and nests (Konštancia vein) penetrating also into ankerite together with abundant pyrite. In cavities in siderite and quartz it forms tiny, max. 1 cm big crystals of tetrahedral form (Raky, Krištof and Konštancia adits). Older sulphides, such as arsenopyrite, pyrite, marcasite, pyrrhotite and sphalerite are replaced by tetrahedrite. It also penetrates into kobellite and jamesonite. In tetrahedrite, apart from needle-shaped grains of kobellite, small grains of gold are locally present. Tetrahedrite aggregates are overgrown by bournonite and bornite. In the mineral succession it is described as the youngest mineral along with chalcopyrite (Bartalský et al., 1962, Bernard, 1958, Matula, 1969, Trdlička, 1963, 1963a, 1963b, 1967, 1967a, Trdlička – Kupka, 1957, Trdlička – Kvaček – Kupka, 1962).

The yet published chemical composition of tetrahedrite from the deposit varies in the following range: Cu 34.77-36.61; Zn 1.15 – 1.76; Fe 6.22 – 7.33; Hg 0.0 – 0.18; Cd tr – 0.01; Sb 26.73 – 29.45; As 0.05 – 0.71; Bi 0.32 – 0.93; S 24.78 – 25.75 wt %; (Konštancia vein); Cu 35.45 – 37.22; Zn 2.93 – 4.73; Fe 3.62 – 4.79; Hg 0.03 – 0.1; Cd 0 – 0.1; Sb 27.72 – 29.06; As 0.51 – 0.59; Bi 0 – 0.14; S 24.5 – 25.53 wt. %; (Krištof vein) (Trdlička, 1967b). Se content was determined in following ranges: 54 – 82 g/t (Babčan, 1966); 0.0054 – 0.0082 wt % (Trdlička, 1963a); 0.002 – 0.0042 wt.% (Kvaček, 1980).

Springer (1969), Hall (1972), Pattrick – Hall (1983), Miller Craig (1983) and others have studied problems of tetrahedrites and tennantites. According to chemical and structural analyses Sack – Loucks (1985) determined the following formula of chemical composition:

$(Cu,Ag)_6\ ([Cu]_{2/3}\ [Fe, Zn, Cd, Hg, Pb]_{1/3})_6\ (Sb, As, Bi)_4\ (S, Se)_{13}$

In this study a general formula:

$$Me^{10}Me^{+2}_{2}(PMe)_4\ S_{13}$$

and the recalculation on the bases of 29 atoms were used. Cu and Ag are considered as monovalent metals (Me^{+1}), Fe, Zn, Hg, Pb, Cd as bivalent metals (Me^{+2}) and Sb, As, Bi, Te as metalloids (PMe) (Charlat – Levy, 1974; Mozgova – Cepin, 1983).

Results of tetrahedrite and tennantite structural study of natural samples were followed by the research of synthesis in systems Cu-Sb-S, Cu-As-S, Cu-Ag-Sb-S, Cu-Fe-Sb-S, performed particularly by Maske – Skinner (1971), Tatsuka – Morimoto (1977), Makovický – Skinner (1978), Sack – Ebel (1993). These authors determined the structure of tetrahedrites and tennantites in an artificial system, along with temperatures of origin and stability of tetrahedrites-tennantites in the range 200 – 500°C.

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Geology and mineralogy of the deposit

The deposit Jedľovec (Fichtenhübel) is located in the central part of the Spišsko-gemerské rudohorie Mts. between the rocks of the Drnava Formation of the Gelnica group (Bartalský et al., 1962; Maheľ, 1954; Reichwalder, 1970). Parallel ore veins form a fan-type stockwork with general direction E-W and steep dip toward south (Fig. 1).

The vein thickness is variable, it changes from 10 cm to 7 m. The vein is known to continue up to 500 m into depth. The ore field Jedľovec forms a system of 8 - 9 siderite-sulphidic veins (dykes) with quartz, such as, from north to south, Kornélia, Konštancia Lower and Upper, Krištof (available by cross cut Raky), Johana, Michal I, II, Daniel I, II, Jozef and a quartz-arsenopyrite vein with Co (Grecula, 1966).

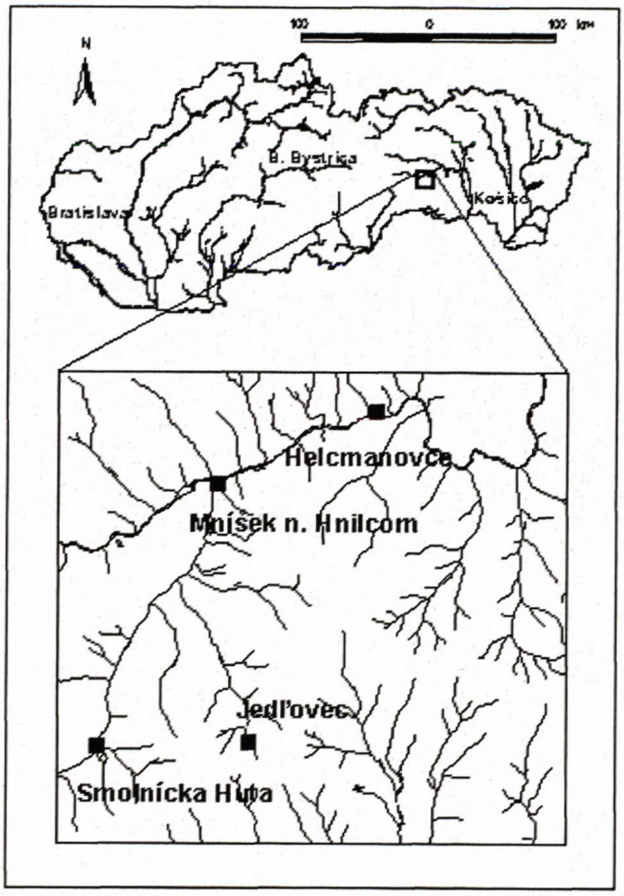

Fig. 1. Location of the deposit Jedľovec.

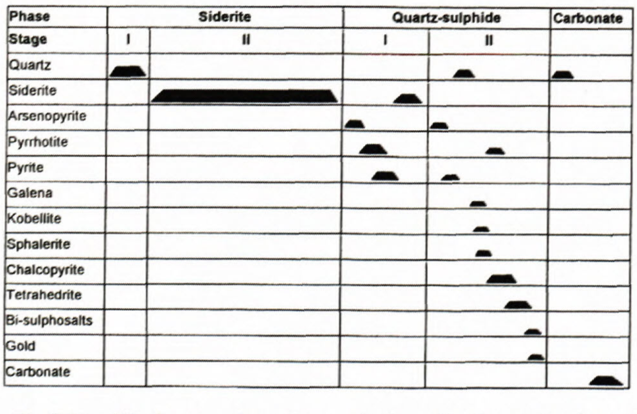

Fig.2.Simplified succession scheme of mineralisation at the deposit Jedľovec (veins Krištof, Konštancia, Michal I), Macinský (1992).

The mineral content of vein filling is quite variegated. It was studied mainly by Drnzíková (in: Grecula - Grosz, 1968; Návesňák, 1967) and Trdlička (1963, 1963a, 1967, 1967a, Trdlička et al., 1962). Coarse-crystalline siderite is the major mineral (Antal, 1996), in which very irregularly located sulphides are present, such as chalcopyrite (Antal, 1997), pyrite, tetrahedrite, arsenopyrite, löllingite, cobaltite, glaucodot, pyrhotite, sphalerite, galena, marcasite, hematite, magnetite, calcite, ankerite, stannite, gold and Bi-sulphosalts (bismuth, aikinite, kobellite, galenobismutite, bournonite, boulangerite, jamesonite) (Macinský and Antal, 1993). Sulphides form irregular veinlets, aggregates, nests, impregnations and disseminations accompanied by milk-white quartz (Fig. 2).

A zonal arrangement of the ore mineralisation was described for the deposit. At the vein Krištof, located in the middle of the fan-type structure of the deposit, the sulphidic mineralisation dominates. In direction to the margin of the fan, formed by veins Konštancia, Daniel and Kornélia, this mineralisation is replaced by the siderite mineralisation. Decrease in sulphides and quartz in direction to margins of these veins manifests the horizontal zoning. The vertical zoning is manifested by the predominance of siderite in upper parts of veins, while sulphides are focused more to the centre. In direction to depth the proportion of ankerite increases simultaneously with sulphide decrease (Matula, 1969; Návesňák et al., 1982).

Veins Konštancia (its western part), Krištof, Michal I and Daniel I. had bigger economic importance. The vein filling of the vein Konštancia is formed by coarse-crystalline siderite with high proportion of quartz. Chalcopyrite and tetrahedrite dominate among sulphides. The vein filling of the vein Krištof is composed of pale-brown siderite, extensively crushed, with breccia-type and impregnation-clustered textures, sealed by sulphides and quartz, with a high chalcopyrite content. The main part of the vein filling of the vein Michal I is formed by siderite with minor amount of sulphides, located in nests. Veins Daniel I and II are formed by coarse- to medium-grained siderite with rare sulphide nests (Fusan - Kantor, 1954; Slávik at al., 1967).

Methodology

A study using a scanning electron microscope (JEOL JSM-840, Geol. Survey of the Slovak Rep. Bratislava, J. Stankovič, D. Dubík) and using an energy dispersive X-ray spectrometer (EDAX, Geol. Survey of the Slovak Rep. Bratislava) preceded quantitative microchemical analyses.

Analyses were carried out on the instrument JEOL SUPERPROBE 733 (Geol. Survey of the Slovak Rep. Bratislava) using a correlation program ZAF-M, 30nA

Tab. 1. Results of microchemical analyses of tetrahedrite [wt.%] from the deposit Jedľovec. Other analysed elements, such as Au, Ni, Co, Pb, Te and Se did not reach detectable concentrations. TD/TN - tetrahedrite number (JEOL SUPERPROBE 733, Geol. Survey of the Slovak Rep. Bratislava, F. Caňo, P. Konečný and P. Siman.)

Veins	**Anal. No.**	**Phase**	**Samp. No.**	**(Cu**	**Ag)**	**(Fe**	**Zn**	**Hg)**	**(Sb**	**As**	**Bi)**	**S**	**Total**	**TD/TN**
			min.	36,43	0,00	3,69	0,00	0,00	24,98	0,00	0,00	21,94	96,28	83,67
			avg.	37,63	0,44	5,05	1,46	0,06	28,49	1,04	0,07	25,25	99,51	94,41
			max.	38,85	1,47	6,01	2,69	0,51	30,11	3,00	0,65	30,02	101,51	100,00
Konštancia	1	3	1	37,93	0,66	4,76	1,47	0,14	29,71	1,03	0,06	23,61	99,37	94,67
Konštancia	2	3	1	37,55	0,74	4,83	1,33	0,19	29,11	1,22	0,00	23,99	98,96	93,62
Konštancia	3	2	1	36,74	0,55	4,85	1,47	0,00	29,93	0,75	0,02	24,82	99,13	96,09
Konštancia	4	1	1	36,95	0,64	5,10	1,26	0,51	27,67	1,96	0,00	24,85	98,94	89,68
Konštancia	5	3	2	37,78	0,20	4,61	1,63	0,29	29,46	0,73	0,02	24,20	98,92	96,13
Konštancia	6	1	2	37,71	0,18	4,97	1,41	0,00	27,38	1,81	0,04	24,59	98,09	90,30
Konštancia	7	1	2	36,66	0,22	5,01	1,38	0,00	27,53	1,83	0,14	25,64	98,41	90,25
Konštancia	8	3	5	36,69	0,53	5,83	0,55	0,00	26,64	0,10	0,39	30,02	100,75	99,39
Konštancia	9	3	6	38,22	0,36	3,84	2,69	0,23	28,39	0,67	0,17	24,59	99,16	96,31
Konštancia	10	undeterm.	6	37,09	0,30	3,69	2,41	0,00	28,27	0,86	0,00	24,97	97,59	95,29
Konštancia	11	3	6	37,83	0,33	3,81	2,59	0,15	28,35	0,65	0,05	25,19	98,95	96,41
Konštancia	12	2	10	38,40	0,00	5,06	1,34	0,00	28,83	0,98	0,00	25,87	100,48	94,77
Konštancia	13	2	10	38,06	0,00	4,97	1,51	0,00	28,87	0,77	0,00	25,56	99,74	95,85
Konštancia	14	3	21	37,61	0,64	5,85	0,63	0,29	30,11	0,00	0,24	23,15	98,52	100,00
Konštancia	15	3	21	36,99	0,72	5,70	0,56	0,23	30,04	0,04	0,06	21,94	96,28	99,78
Konštancia	16	2	25	37,90	0,00	4,69	1,73	0,00	29,00	0,83	0,00	26,05	100,20	95,56
Konštancia	17	2	25	38,32	0,00	4,64	1,92	0,00	29,04	1,05	0,00	25,64	100,61	94,45
Konštancia	18	1	27	38,59	0,00	5,69	0,48	0,00	28,11	1,31	0,00	25,53	99,71	92,96
Konštancia	19	1	27	38,85	0,00	6,01	0,00	0,00	28,18	1,96	0,00	26,51	101,51	89,85
Konštancia	20	2	27	38,36	0,00	6,01	0,51	0,00	29,02	0,91	0,00	25,38	100,19	95,15
Konštancia	21	1	27	38,10	0,00	5,94	0,19	0,00	27,50	2,02	0,00	26,02	99,77	89,34
Konštancia	22	1	28	38,29	0,00	5,31	0,98	0,00	26,96	1,66	0,00	26,16	99,36	90,90
Konštancia	23	1	28	38,52	0,00	5,43	0,97	0,00	27,01	1,64	0,00	26,08	99,65	91,02
Konštancia	24	1	28	38,79	0,00	5,29	1,01	0,00	28,20	1,15	0,00	26,00	100,44	93,78
Konštancia	25	3	37	38,01	0,37	5,19	1,36	0,21	26,76	2,47	0,65	24,49	99,51	86,96
Konštancia	26	3	37	38,15	0,38	5,23	1,33	0,21	29,51	0,56	0,51	23,90	99,78	97,01
Konštancia	27	3	37	38,12	0,37	4,88	1,74	0,33	29,64	0,46	0,39	24,04	99,97	97,54
Konštancia	28	3	37	38,36	0,36	4,77	1,87	0,21	29,29	0,56	0,42	24,49	100,33	96,99
Konštancia	29	3	37	38,80	0,40	5,40	1,40	0,12	26,64	2,70	0,55	24,31	100,32	85,86
Konštancia	30	1	38	37,62	0,36	4,69	1,92	0,00	27,07	1,72	0,00	26,25	99,63	90,64
Konštancia	31	1	38	38,49	0,24	4,60	1,90	0,00	24,98	3,00	0,00	26,34	99,55	83,67
Konštancia	32	1	55	37,54	0,00	5,00	1,70	0,00	28,92	1,56	0,00	25,83	100,55	91,94
Konštancia	33	1	55	37,86	0,02	4,94	1,75	0,00	27,67	1,37	0,00	25,81	99,42	92,55
Krištof	34	1	4	37,65	0,00	5,37	2,22	0,00	25,11	2,80	0,00	26,38	99,53	84,66
Krištof	35	undeterm.	4	37,22	0,00	5,06	2,52	0,00	27,36	1,19	0,00	25,76	99,11	93,40
Krištof	36	2	18	37,08	0,42	4,23	2,30	0,00	29,04	0,45	0,00	25,60	99,12	97,54
Krištof	37	2	18	36,97	0,51	4,12	2,57	0,00	29,76	0,48	0,00	25,31	99,72	97,45
Krištof	38	2	18	37,43	0,42	4,24	2,66	0,00	29,11	0,45	0,00	25,65	99,96	97,55
Krištof	39	2	40	36,43	1,16	5,89	0,38	0,00	28,72	0,73	0,00	25,85	99,16	96,03
Krištof	40	2	40	37,36	1,18	5,65	0,63	0,00	28,84	0,73	0,00	26,18	100,57	96,05
Krištof	41	3	45	38,25	0,43	5,63	0,97	0,00	29,91	0,71	0,09	22,41	98,40	96,29
Krištof	42	3	45	37,70	0,44	5,63	1,01	0,04	29,35	0,91	0,01	23,59	98,68	95,20
Krištof	43	2	46	37,29	0,14	5,47	0,72	0,00	28,83	0,19	0,00	25,73	98,37	98,94
Krištof	44	2	46	37,17	0,12	5,68	0,77	0,00	29,93	0,31	0,00	25,61	99,59	98,34
Krištof	45	2	49	36,83	1,05	5,16	1,72	0,00	28,50	0,84	0,00	25,83	99,93	95,43
Krištof	46	2	49	36,60	1,47	4,88	1,69	0,00	29,73	0,66	0,00	25,33	100,36	96,52
Krištof	47	2	49	37,07	1,36	5,01	1,69	0,00	28,77	0,64	0,00	25,25	99,79	96,51
Krištof	48	2	49	36,75	1,22	4,83	1,90	0,00	29,16	0,20	0,00	25,24	99,30	98,90
Krištof	49	2	49	36,50	1,33	4,32	2,34	0,00	29,49	0,29	0,00	24,91	99,18	98,43
Krištof	50	2	49	37,25	1,38	4,90	1,56	0,00	28,74	0,71	0,00	26,37	100,91	96,14
Krištof	51	2	49	36,78	1,31	4,98	1,66	0,00	28,94	0,55	0,00	25,18	99,40	97,00
Konštancia			**avg.**	37,91	0,26	5,05	1,36	0,09	28,30	1,22	0,11	25,21	99,51	93,48
Krištof			**avg.**	37,13	0,77	5,06	1,63	0,00	28,85	0,71	0,01	25,34	99,50	96,13

Tab. 2. Calculated atomic ratios of crystallochemical formulas of tetrahedrite from the deposit Jedľovec. (A – Me+1, B – Me+2, A+B – total Me, C – PMe)

Veins	Anal. No.	Phase	Samp. No.	Cu	Ag	A	Fe	Zn	Fe+Zn	Hg	B	A+B	Sb	As	Bi	C	S	ABCD	TD/TN
Konštancia	1	3	1	10,15	0,00	10,25	1,45	0,38	1,83	0,01	1,84	12,09	4,15	0,23	0,00	4,39	12,52	29	94,7
Konštancia	2	3	1	10,03	0,00	10,14	1,47	0,35	1,81	0,02	1,83	11,97	4,06	0,28	0,00	4,33	12,70	29	93,6
Konštancia	3	2	1	9,73	0,00	9,82	1,46	0,38	1,84	0,00	1,84	11,66	4,14	0,17	0,00	4,31	13,03	29	96,1
Konštancia	4	1	1	9,75	0,00	9,85	1,53	0,32	1,85	0,04	1,90	11,75	3,81	0,44	0,00	4,25	13,00	29	89,7
Konštancia	5	3	2	10,07	0,00	10,10	1,40	0,42	1,82	0,02	1,85	11,95	4,10	0,17	0,00	4,27	12,79	29	96,1
Konštancia	6	1	2	9,99	0,00	10,02	1,50	0,36	1,86	0,00	1,86	11,88	3,79	0,41	0,00	4,20	12,92	29	90,3
Konštancia	7	1	2	9,61	0,00	9,65	1,49	0,35	1,85	0,00	1,85	11,49	3,77	0,41	0,01	4,19	13,32	29	90,3
Konštancia	8	3	5	9,03	0,00	9,11	1,63	0,13	1,76	0,00	1,76	10,88	3,42	0,02	0,03	3,47	14,65	29	99,4
Konštancia	9	3	6	10,11	0,00	10,16	1,16	0,69	1,85	0,02	1,87	12,03	3,92	0,15	0,01	4,08	12,89	29	96,3
Konštancia	10	undeterm.	6	9,89	0,00	9,93	1,12	0,62	1,74	0,00	1,74	11,68	3,93	0,19	0,00	4,13	13,19	29	95,3
Konštancia	11	3	6	9,95	0,00	10,00	1,14	0,66	1,80	0,01	1,82	11,82	3,89	0,15	0,00	4,04	13,14	29	96,4
Konštancia	12	2	10	9,89	0,00	9,89	1,48	0,34	1,82	0,00	1,82	11,71	3,87	0,21	0,00	4,09	13,20	29	94,8
Konštancia	13	2	10	9,89	0,00	9,89	1,47	0,38	1,85	0,00	1,85	11,74	3,92	0,17	0,00	4,09	13,17	29	95,8
Konštancia	14	3	21	10,19	0,00	10,29	1,80	0,17	1,97	0,02	1,99	12,29	4,26	0,00	0,02	4,28	12,43	29	100,0
Konštancia	15	3	21	10,34	0,00	10,46	1,81	0,15	1,97	0,02	1,99	12,45	4,38	0,01	0,01	4,40	12,16	29	99,8
Konštancia	16	2	25	9,78	0,00	9,78	1,38	0,43	1,81	0,00	1,81	11,59	3,91	0,18	0,00	4,09	13,32	29	95,6
Konštancia	17	2	25	9,89	0,00	9,89	1,36	0,48	1,84	0,00	1,84	11,74	3,91	0,23	0,00	4,14	13,12	29	94,5
Konštancia	18	1	27	10,00	0,00	10,00	1,68	0,12	1,80	0,00	1,80	11,80	3,80	0,29	0,00	4,09	13,11	29	93,0
Konštancia	19	1	27	9,83	0,00	9,83	1,73	0,00	1,73	0,00	1,73	11,56	3,72	0,42	0,00	4,14	13,30	29	89,8
Konštancia	20	2	27	9,94	0,00	9,94	1,77	0,13	1,90	0,00	1,90	11,84	3,92	0,20	0,00	4,12	13,04	29	95,2
Konštancia	21	1	27	9,81	0,00	9,81	1,74	0,05	1,79	0,00	1,79	11,59	3,69	0,44	0,00	4,13	13,27	29	89,3
Konštancia	22	1	28	9,86	0,00	9,86	1,56	0,25	1,80	0,00	1,80	11,66	3,62	0,36	0,00	3,99	13,35	29	90,9
Konštancia	23	1	28	9,90	0,00	9,90	1,59	0,24	1,83	0,00	1,83	11,73	3,62	0,36	0,00	3,98	13,29	29	91,0
Konštancia	24	1	28	9,95	0,00	9,95	1,54	0,25	1,80	0,00	1,80	11,75	3,78	0,25	0,00	4,03	13,22	29	93,8
Konštancia	25	3	37	9,99	0,00	10,05	1,55	0,35	1,90	0,02	1,92	11,97	3,67	0,55	0,05	4,27	12,76	29	87,0
Konštancia	26	3	37	10,14	0,00	10,20	1,58	0,34	1,93	0,02	1,94	12,14	4,09	0,13	0,04	4,26	12,59	29	97,0
Konštancia	27	3	37	10,11	0,00	10,17	1,47	0,45	1,92	0,03	1,95	12,12	4,10	0,10	0,03	4,24	12,64	29	97,5
Konštancia	28	3	37	10,08	0,00	10,14	1,43	0,48	1,90	0,02	1,92	12,06	4,02	0,12	0,03	4,18	12,76	29	97,0
Konštancia	29	3	37	10,13	0,00	10,19	1,60	0,36	1,96	0,01	1,97	12,16	3,63	0,60	0,04	4,27	12,57	29	85,9
Konštancia	30	1	38	9,68	0,00	9,74	1,37	0,48	1,85	0,00	1,85	11,59	3,64	0,38	0,00	4,01	13,39	29	90,6
Konštancia	31	1	38	9,83	0,00	9,87	1,34	0,47	1,81	0,00	1,81	11,68	3,33	0,65	0,00	3,98	13,34	29	83,7
Konštancia	32	1	55	9,68	0,00	9,68	1,47	0,43	1,89	0,00	1,89	11,57	3,89	0,34	0,00	4,23	13,20	29	91,9
Konštancia	33	1	55	9,81	0,00	9,81	1,46	0,44	1,90	0,00	1,90	11,71	3,74	0,30	0,00	4,04	13,25	29	92,6
Krištof	34	1	4	9,60	0,00	9,60	1,56	0,55	2,11	0,00	2,11	11,71	3,34	0,61	0,00	3,95	13,34	29	84,7
Krištof	35	undeterm.	4	9,66	0,00	9,66	1,49	0,64	2,13	0,00	2,13	11,79	3,70	0,26	0,00	3,97	13,25	29	93,4
Krištof	36	2	18	9,72	0,00	9,78	1,26	0,59	1,85	0,00	1,85	11,63	3,97	0,10	0,00	4,07	13,30	29	97,5
Krištof	37	2	18	9,70	0,00	9,78	1,23	0,66	1,88	0,00	1,88	11,66	4,07	0,11	0,00	4,18	13,16	29	97,4
Krištof	38	2	18	9,73	0,00	9,80	1,25	0,67	1,93	0,00	1,93	11,73	3,95	0,10	0,00	4,05	13,22	29	97,5
Krištof	39	2	40	9,52	0,00	9,69	1,75	0,10	1,85	0,00	1,85	11,54	3,92	0,16	0,00	4,08	13,38	29	96,0
Krištof	40	2	40	9,62	0,00	9,80	1,65	0,16	1,81	0,00	1,81	11,61	3,87	0,16	0,00	4,03	13,36	29	96,0
Krištof	41	3	45	10,41	0,00	10,48	1,74	0,26	2,00	0,00	2,00	12,48	4,25	0,16	0,01	4,42	12,09	29	96,3
Krištof	42	3	45	10,10	0,00	10,17	1,72	0,26	1,98	0,00	1,98	12,16	4,11	0,21	0,00	4,31	12,53	29	95,2
Krištof	43	2	46	9,79	0,00	9,81	1,63	0,18	1,82	0,00	1,82	11,62	3,95	0,04	0,00	3,99	13,38	29	98,9
Krištof	44	2	46	9,70	0,00	9,72	1,69	0,20	1,88	0,00	1,88	11,60	4,08	0,07	0,00	4,15	13,25	29	98,3
Krištof	45	2	49	9,56	0,00	9,72	1,52	0,43	1,96	0,00	1,96	11,67	3,86	0,18	0,00	4,04	13,28	29	95,4
Krištof	46	2	49	9,57	0,00	9,79	1,45	0,43	1,88	0,00	1,88	11,67	4,06	0,15	0,00	4,20	13,12	29	96,5
Krištof	47	2	49	9,70	0,00	9,91	1,49	0,43	1,92	0,00	1,92	11,83	3,93	0,14	0,00	4,07	13,10	29	96,5
Krištof	48	2	49	9,67	0,00	9,86	1,45	0,49	1,93	0,00	1,93	11,79	4,00	0,04	0,00	4,05	13,16	29	98,9
Krištof	49	2	49	9,67	0,00	9,88	1,30	0,60	1,90	0,00	1,90	11,78	4,08	0,07	0,00	4,14	13,08	29	98,4
Krištof	50	2	49	9,56	0,00	9,77	1,43	0,39	1,82	0,00	1,82	11,59	3,85	0,15	0,00	4,00	13,41	29	96,1
Krištof	51	2	49	9,67	0,00	9,87	1,49	0,42	1,91	0,00	1,91	11,79	3,97	0,12	0,00	4,09	13,12	29	97,0

beam current, 25kV accelerating voltage, LiF crystal and following standards: pure Cu, Ag, Fe, Zn, Co, Ni, Bi, Sb, Te, Au, cinnabar for Hg, arsenopyrite for As and S, Bi_2Se_3 for Se. Operators were F. Caňo, P. Konečný and P. Siman.

Measurements were performed on polished, degreased and ultrasonic-cleaned sections and polished sections, coated by carbon. Apart from elements shown in tables 1 and 2 also some other elements, such as Au, Ni, Co, Pb, Te and Se were measured, but they did not reach detectable concentrations.

Crystallochemical formulas of tetrahedrites were recalculated according to the basic structure of the cell $Me^{+1}10$, $Me^{+2}2$, PMe4, S13. This represents 29 atoms per unit cell.

Mineralogy and geochemistry of tetrahedrites

In the studied samples tetrahedrite forms irregular aggregates, often associated with chalcopyrite in quartz or siderite veinstone. It contains tiny grains of arsenopyrite or pyrite, often idiomorphous, locally with a slightly cataclastic texture. Tetrahedrite as one of the youngest minerals (Fig. 2) cuts older minerals by a network of veinlets, or it seals cataclased minerals along fractures.

The chemical composition, determined by microanalyses, showed that the studied tetrahedrite is an Sb-end member of the tetrahedrite-tennantite isomorphous series, containing from 83.67 to 100 % of the tetrahedrite component. Fe reaches more significant concentrations (from 1.81 at.%, respect. 6.01 wt.%) at the expense of Zn (from 0 to 0.69 at.%, respect. from 0 to 2.69 wt.%).

Maximum concentrations of minor elements vary around 1.47 wt.% for Ag, 0.65 wt.% for Bi and 0.51 wt.% for Hg (Tab. 1 and 2).

Generally, the chemical composition of tetrahedrite from the deposit Jedľovec (from veins – Konštancia and Krištof) can be characterised as Fe-tetrahedrite.

Nearly all analyses showed an excess of metalloids (PMe) and a significant predominance of Sb over As and a lack of bivalent metals compared to the theoretical composition (Me^{+2}, Fe>Zn). Concentration of metalloids (represented by sulphur only) and monovalent metals (Me^{+1}, Cu>>Ag) also ranges over the theoretical composition of tetrahedrite.

Mutual relationship among groups of elements forming aggregates of tetrahedrite (Me^{+1}, Me^{+2}, PMe, S) and elements themselves are diverse. In the literature discussed negative relationships are preserved between Sb : As, Fe : Zn and Cu : Ag only (Johnson, Craig & Rimstidt, 1986; Mozgova & Cepin, 1983).

Negative mutual relationship, expressed also by the coefficient of correlation, have also two major groups of tetrahedrite elements PMe and S. An increase in PMe content, resulting in PMe excess, is simultaneous to the decrease of S concentration, that gets below the theoretical value of S concentration in tetrahedrite (Fig. 3A). This trend is the result of relatively different behaviour of Sb and As to S. A higher concentration of the earlier (Sb) is accompanied by a decrease of the S content (Fig. 3B) and on the contrary, an increase in As content is accompanied by an increase in S concentration. Because Sb contents in absolute values are significantly higher, a negative relationship of Sb to S prevails in the total of PMe.

A negative relationship occurs also between S content and contents of metals, monovalent (Me^{+1} – Cu, Ag, Fig. 3C) and partly also bivalent ones (Me^{+2} – Fe, Zn).

The relationship between Ag and S values is preserved apart from samples with high concentration of Ag (samples no. 40, 49) (Fig. 3D). Cu and S values (Fig. 4A) form a less apparent negative relationship. Even positive trends are possible to reach, if the field of data points is divided according to samples from individual veins.

In the mutual relationship between S and Me^{+1} (r – 0.99) these relatively conflicting relationships of studied elements were manifested in a not very clear negative trend (r –0.5) in samples with S content over, and Me^{+1} below the theoretical composition, compared to the significant trend outside these values (r –0.9) (Fig. 3C).

Equally negative relationship between Me^{+2} and S (r – 0.43) is more apparent if the individual elements are confronted with sulphur. When the data field is divided according to sulphur values, two types of values (samples) are possible to assign at Fe : S and Zn : S diagrams. One group has a stable concentration of S and an increasing or decreasing content of Fe or Zn. The second group has decreasing concentration of S and increasing Fe or decreasing Zn contents (Fig. 4C). These relationships are included also in a comprehensive diagram S : Me^{+2}, where a field of samples with a constant S content is possible to assign (slightly in excess, r –0.13), together with a field of samples with decreasing S content (r –0.72) and relatively increasing values of Me^{+2} (Fig. 4B).

Me and PMe contents show a positive relationship (Fig. 4. D). This trend is preserved in the relationship between PMe and Me^{+1} (r 0.76), but in the relationship with Me^{+2} a spread of values occurs (r 0.25), while just one sample exceeds the value of the theoretical composition (sample no. 4). The positive trend between Me^{+1} and PMe is formed by the predominance of Cu values and by the positive trend of As and Ag to Sb (Fig. 5A). The relationship between Cu and Sb is not distinct and it is more characterised by a large scatter of values. The relationship between As and Ag is negative (Fig. 5B), but due to significantly lower values of Ag compared to Cu the positive relationship between PMe and Me^{+1} was not affected.

Very weak mutual relationship between PMe and Me^{+2} is preserved also in relations of individual elements.

Me^{+1} values with Me^{+2} values form a weak positive relationship (r 0.,07) (Fig. 5C). Relatively larger spread of values is the result of weak positive relationship of majority metals (Cu and Fe) and relatively neutral relationship between Cu and Zn, Ag and Fe, Ag and Zn.

Concernig minor elements, tetrahedrites from the Jedľovec deposit contain smaller amount of Ag and Hg. Hg shows usually zero content and its maximum concentration reaches 0.51 wt.%. Because at such low concentration a relatively high analytical error occurs a work with absolute values is not possible.

The concentration of silver varies from 0 to 1.47 wt. %, while the average value is higher in samples from the

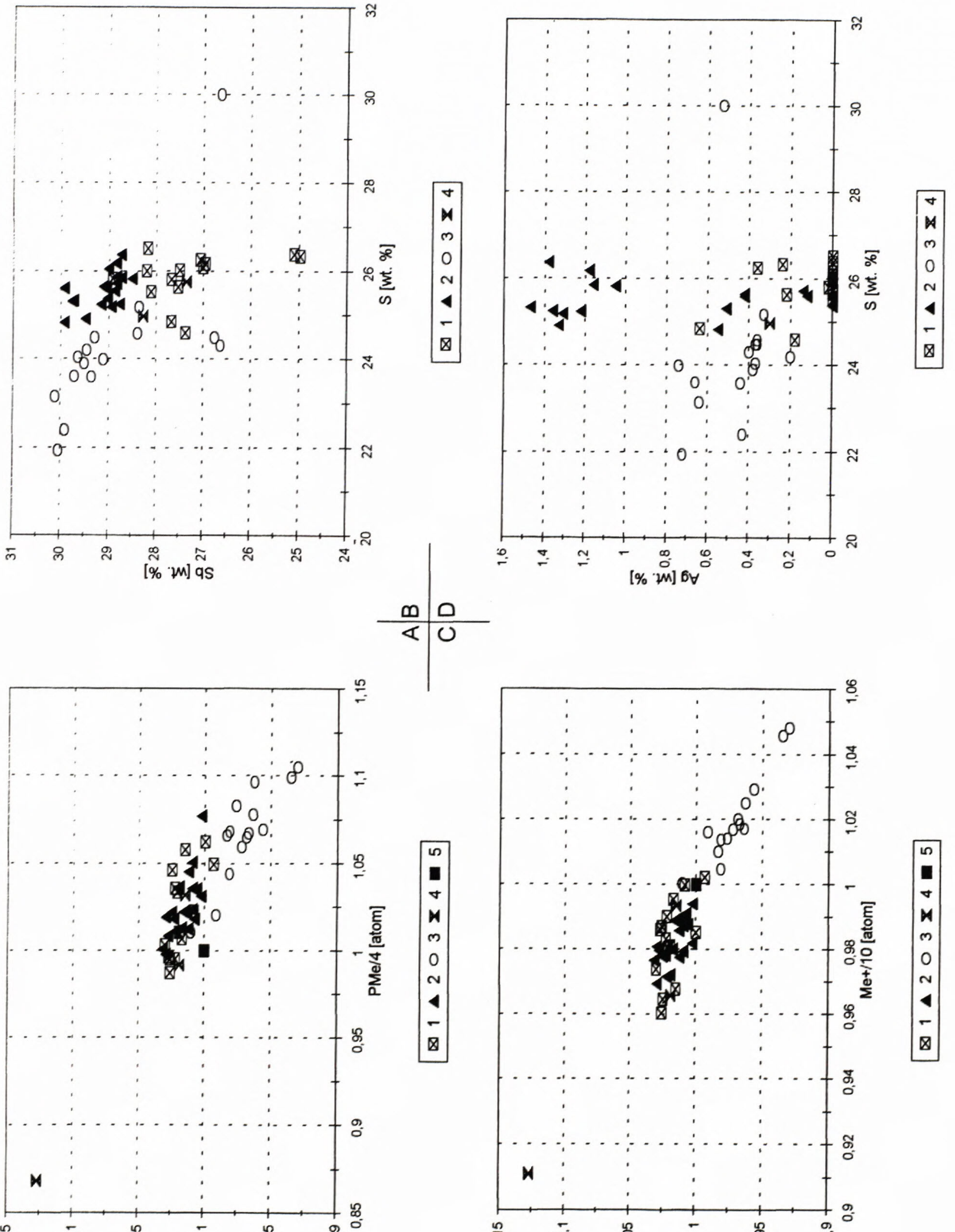

Fig. 3. Correlation diagrams of chemical composition of tetrahedrite from the deposit Jedl'ovec. (1 – first phase of the I. generation Cu-As, 2 – second phase of the I. generation Sb-Ag, 3 – phases of the II. generation Hg-Bi, 4 – not assigned phases, 5 – theoretical composition).

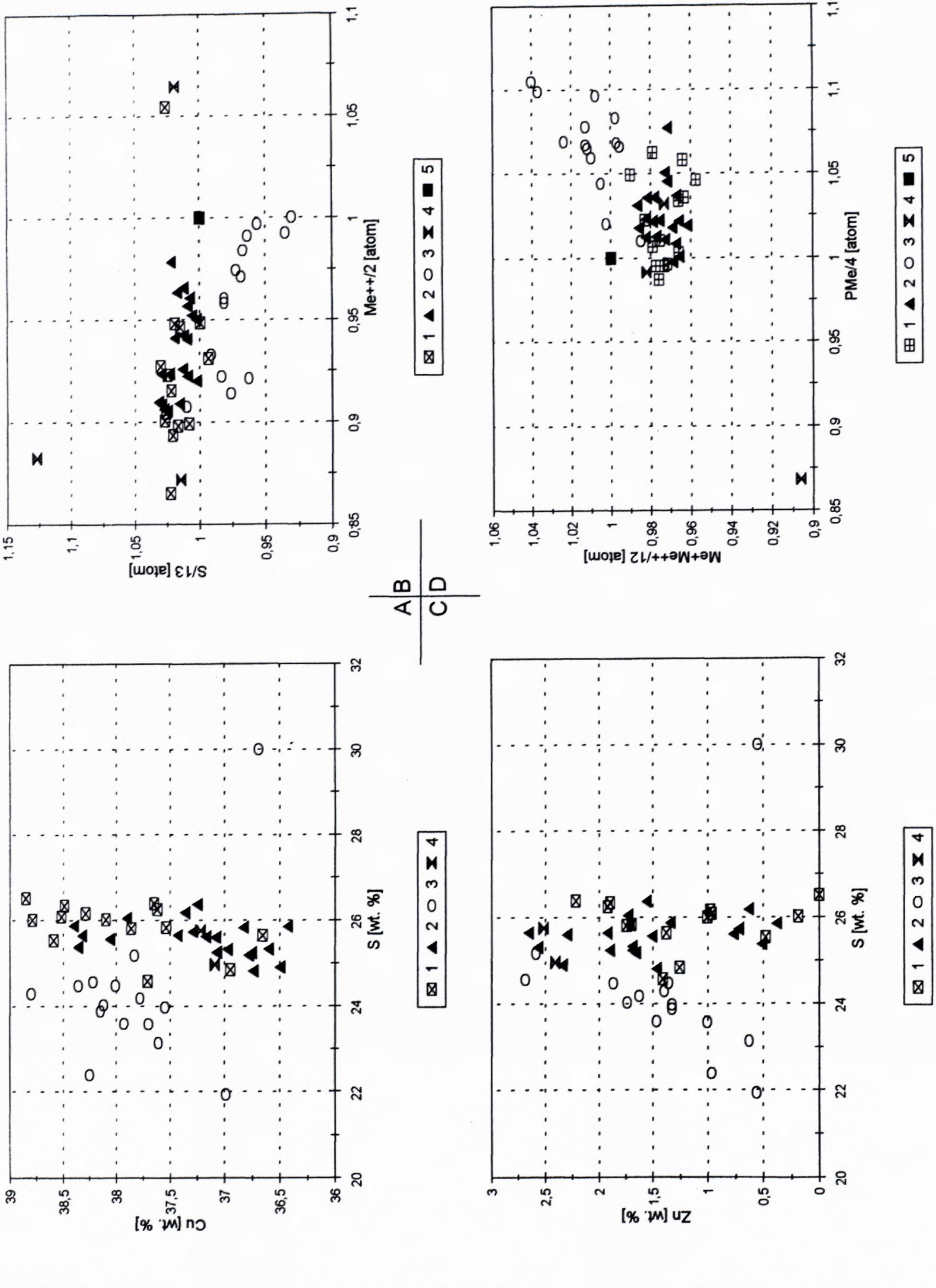

Fig. 4. Correlation diagrams of chemical composition of tetrahedrite from the deposit Jedl'ovec. (1 – first phase of the I. generation Cu-As, 2 – second phase of the I. generation Sb-Ag, 3 – phases of the II. generation Hg-Bi, 4 – not assigned phases, 5 – theoretical composition).

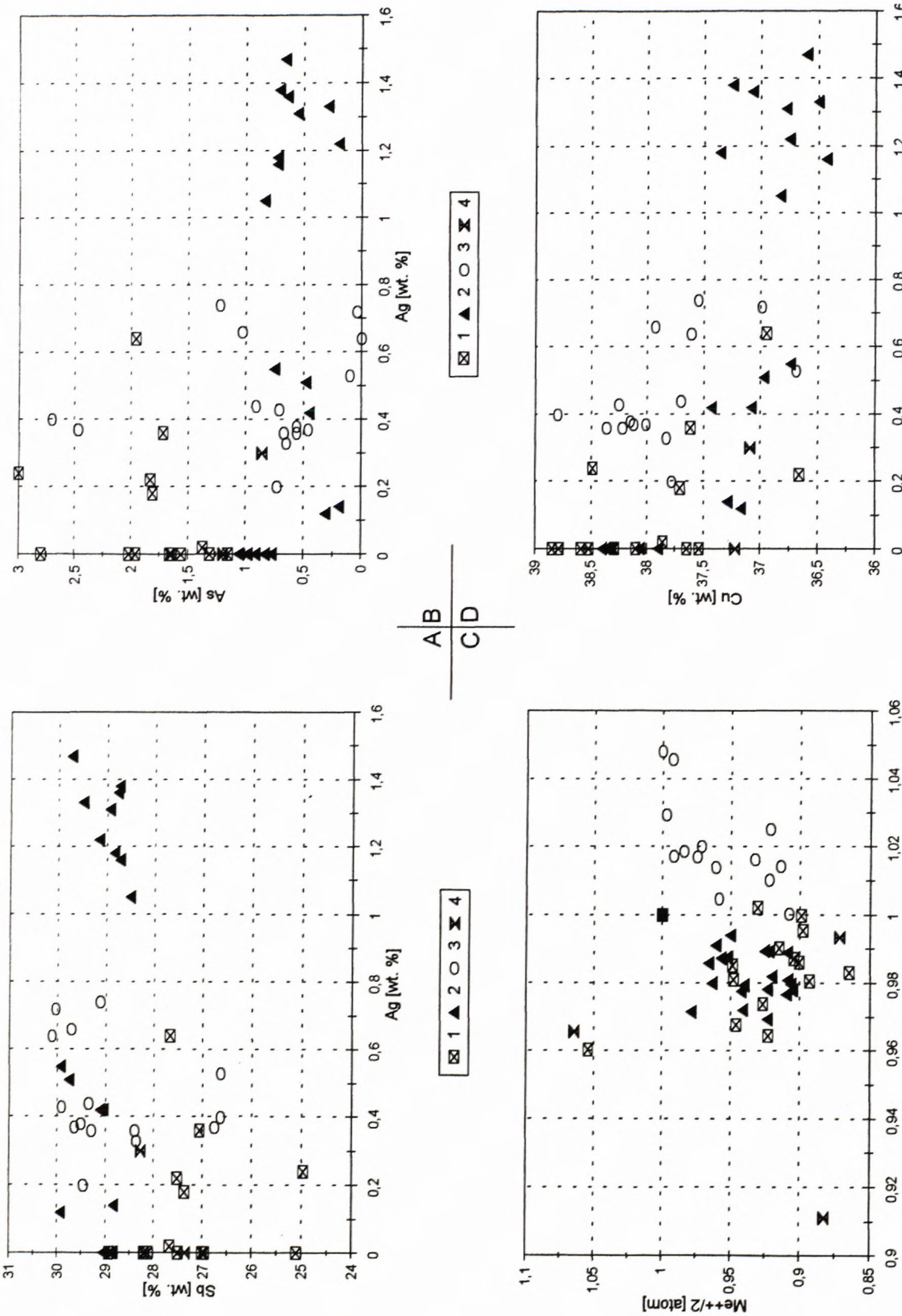

Fig. 5. Correlation diagrams of chemical composition of tetrahedrite from the deposit Jedľovec. (1 – first phase of the I. generation Cu-As, 2 – second phase of the I. generation Sb-Ag, 3 – phases of the II. generation Hg-Bi, 4 – not assigned phases, 5 – theoretical composition).

vein Krištof (0.77 wt. %) than from the vein Konštancia (0.26 wt. %) (Tab. 1).

The relationship of Ag and Me^{+2} is not possible to define unambiguously. Values have a large spread, while only samples with high Ag content from the vein Krištof are more distinctly detached.

Apart from samples with high Ag content, a negative trend between concentrations of Ag and S occurs within the frame of the analytical set (Fig. 3D). The relatively increasing concentration of Ag is accompanied by a decrease of S content.

Values of S concentration in samples from the vein Krištof vary around 26 wt. % (apart from samples no. 45; 22.41 – 23.59 wt. %).

The relationship between Ag and As also show a negative trend, accompanied by the selection of samples with high content of Ag (samples no. 40, 49) and low concentration of As. Ag and Sb show a reverse mutual relationship (Fig. 5A, B).

Generally it is possible to say that an increase in Ag concentration is accompanied also by an increase of Sb and decrease of Cu. Fe, Zn and S concentrations are variable – over and below theoretical values. Tetrahedrites with high concentration of Ag are possible to characterise as mineral aggregates with high contents of S and Sb and low contents of As and Cu (Fig. 5D). These samples with higher concentration of Ag are located at the vein Krištof.

The data field, representing chemical composition of analysed phases of tetrahedrites from the deposit Jedľovec, is possible to divide into 3 groups, according to the following typical features:

The 1st group of phases, in majority of samples, has typically higher concentration of Cu (cca over 37.5 wt. %) and As (cca over 1.25 wt. %) within the frame of studied set of analyses. Simultaneously lower concentration of Sb (cca < 28.5 wt. %) and Ag (cca < 0.4 wt. %) is typical, while the 2nd group of phases again has higher Sb and Ag contents (over the values shown, figs. 3B, 4A, 5A, D).

Compared to the 3rd group of phases the 1st and 2nd groups contain high concentration of S, that is always over the theoretical value and they show a low scatter of values (Fig. 3A, B, 4 A). The total of monovalent metals is always below the theoretical value, similar is the concentration of Me^{+2} (Fig. 3C, 4B).

3rd group of phases shows a lack of S and a high scatter of other elements concentrations. The total of Me^{+1}, represented predominantly by Cu, is mostly in excess and over the theoretical value of 10 atoms (Fig. 3C, 4D). Compared to the 1st and 2nd group of phases it contains higher values of PMe total (Fig. 3A). Furthermore, among several elements an apparent correlation occurs, either positive (Zn : S, Me : PMe, Me^{+1}: Me^{+2}) or negative (Fe : S).

Ag and relatively also As reach higher concentrations in the 1st and the 2nd group of elements (Fig. 5B). Hg and Bi contents are bounded to the 3rd group.

Samples with tetrahedrite phases belonging to the 1st and 2nd group are present in both studied veins. At the vein Krištof only two phases from the 2nd group are characterised by Sb and Ag contents (apart from the sample no. 4). At the vein Konštancia phases of this composition are present in upper parts of the vein and in its E part. Phases typical by Cu and As contents are located in W margin, central and lower parts of the vein.

Phases representing the 3rd group (with Hg and Bi) markedly occur at the vein Konštancia. Here they concentrate mainly in the central part of the vein, forming a narrow zone that reaches from the centre of the vein up to its upper part in vertical direction. Just one sample from the vein Krištof belongs to the 3rd group (Fig. 6).

Homogenity of tetrahedrite aggregates

The variability of tetrahedrite aggregates composition is manifested in their inhomogenity too. Inhomogeneous aggregates with several types of structures occur among relatively large number of homogeneous aggregates. Cloddy and stockwork textures are the most common types of textures (Fig. 7). Both textures consist of phases forming irregular bodies or a network of tetrahedrite veinlets of variable thickness, irregularly cutting the basic phase of the tetrahedrite aggregate. Rarely, regular, banded-laminated structures occur, representing incremental zones of variable composition. These zones rim the aggregates with cloddy texture and simultaneously they are cut by a network of tetrahedrite veinlets. Cloddy textures were observed in samples from both studied veins, but the stockwork texture just in samples from the vein Konštancia and its central part.

Discussion

Apart from textural-structural features, we suppose that two generations of tetrahedrite formation occurred. The younger generation corresponds to the 3rd group of phases with Hg, Bi contents (Spiridonov – Badalov, 1983; Spiridonov et al., 1990), high concentrations of Me^{+1} (Tarkian – Breskovskaja 1990; Spiridonov – Badalov, 1983; Spiridonov et al., 1990) and low S content (Lynch, 1989). Sulphur deficiency as well as an excess of Me^{+1} can correspond to an increase in redox potential of the environment (Spiridonov – Badalov, 1983;), while a part of Cu becomes bivalent.

Based on the frequent similarity of chemical composition proportions to phases of the 1st generation we suppose that phases of the 2nd generation included also the chemical composition of older phases. Alternatively, younger solutions with Hg, Bi, Cu and Sb contents were „contaminated“ by these phases.

Only the chemical composition of the sample no. 6 does not show any relation to elements of older phases. Its position in the centre of the zone formed by phases of the 2nd generation could be understood as a representative of this generation with a non-affected chemical composition.

Different chemical composition of the selected generations is manifested also in mutual relationships of individual major elements forming the studied tetrahedrites. The biggest differences occur in relations with sulphur. The biggest difference between the selected generations was determined in the relationship of Me^{+2} (1. gen. r –0.13, 2. gen. r –0.72) and Me^{+1} (1. gen. r –0.13, 2. gen. r –0.72).

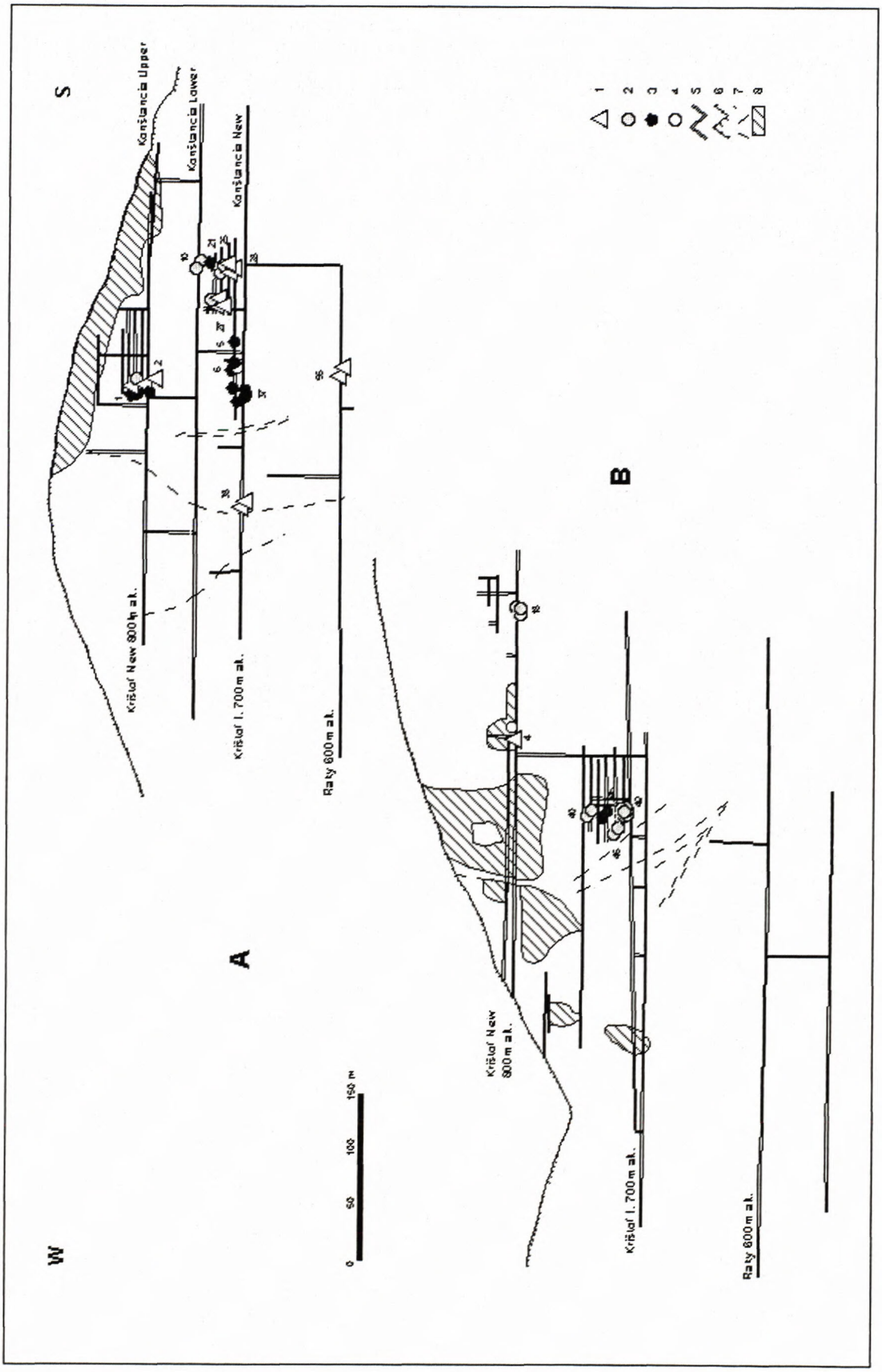

Fig. 6. Map of location of samples with analysed phases from the deposit Jedľovec. A – vein Konštancia, B – vein Krištof (1 – first phase of the I. generation Cu-As, 2 – second phase of the I. generation Sb-Ag, 3 – phases of the II. generation Hg-Bi, 4 – not assigned phases, 5 – mining galleries, 6 – surface line, 7 – faults, 8 – worked-out spaces).

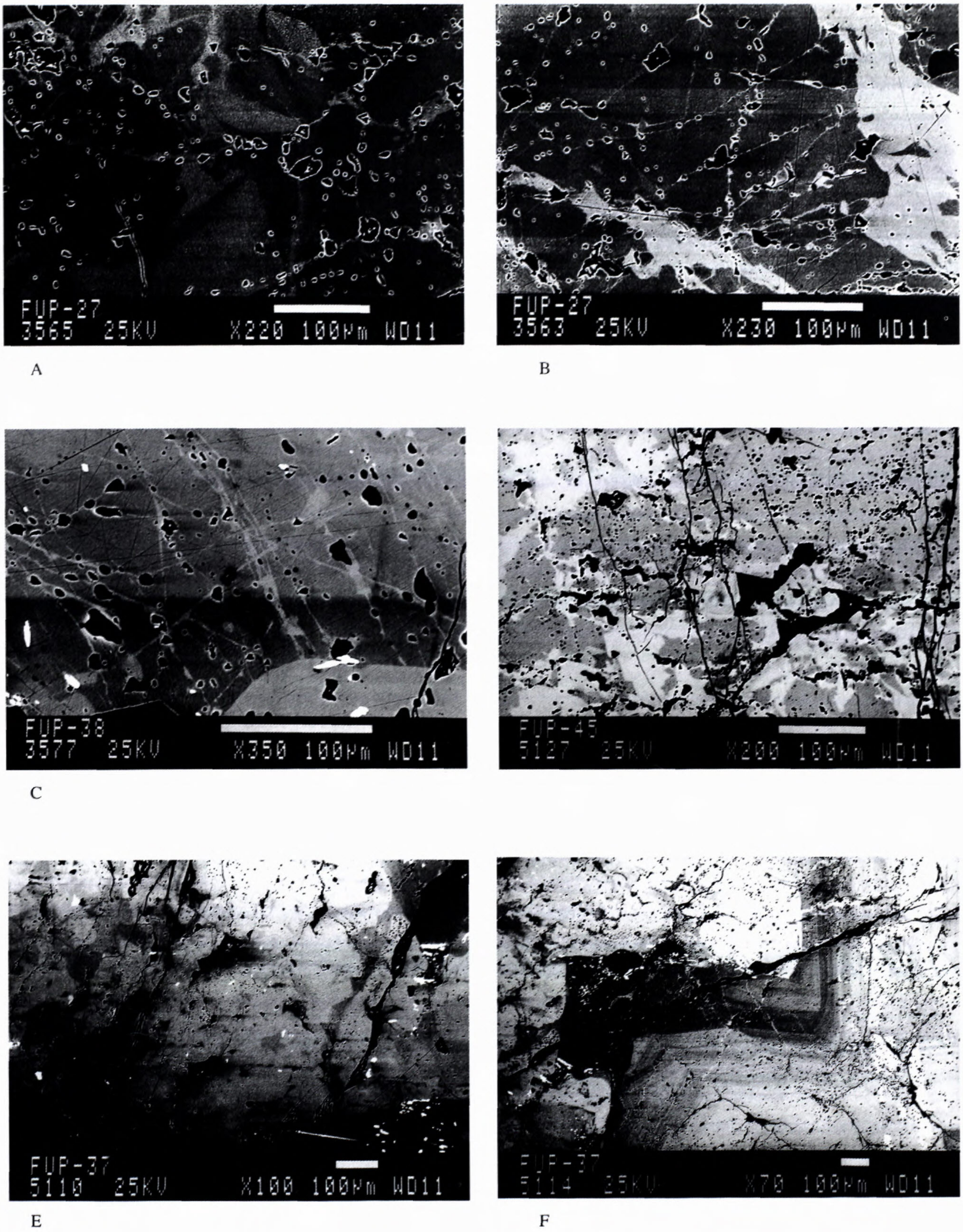

Fig. 7. Examples of inhomogenity textures of tetrahedrite aggregates from the deposit Jedl'ovec. A – spotty texture; A, B, C – stockwork texture; D, E – spotty "cloddy" texture; F – an aggregate with spotty texture rims a zone formed by banded texture.

Similar differences occur also in relationships of PMe and Me^{+1} (1. gen. r –0.01, 2. gen. r +0.67) as well as Me^{+2} (1. gen. r –0.1, 2. gen. r +0.44). Differences between generations occur also in Me^{+1} and Me^{+2} relationship (1. gen. r +0.05, 2. gen. r 0.6).

Older generation, composed of phases of the 1st and the 2nd group, forms a geochemical zoning represented by phases typical of Cu, As and Sb + Ag contents. The position of phases with increased concentrations of Cu and As should be close to the source of solutions (Hackbarth – Petersen, 1984; Mishra – Mookherjee, 1991; Petersen et al., 1990). Phases with Sb and Ag contents should originate in peripheral parts of veins, in zones remote from the source of solutions.

As shown above, mining works at the vein Krištof reached its peripheral part with Sb, Ag phases. At the vein Konštancia probably also an area was accessed, where solutions were introduced into the structure. This is supported also by the location of the younger 2nd generation with Hg and Bi contents (fig 6).

Conclusions

1. At the deposit Jedľovec (veins Krištof, Konštancia) Fe-tetrahedrite was determined, containing from 100 to 83,67% of the tetrahedrite component with negligible concentration of accompanying metals.

2. Based on chemical composition of individual phases, forming aggregates, two generations of tetrahedrite have been distinguished:

2. a. older, with high and stable concentration of S and lower contents of PMe, Me^{+1} and Me^{+2}, higher concentration of Sb and the presence of high concentrations of Ag within the frame of the set of analyses. This generation is formed by two geochemically dicriminable phases that are typical by the presence of the following metal associations: 1 – Cu, As and 2 – Sb, Ag.

2. b. younger generation typically has present Hg and Bi, sulphur deficiency and high concentrations of Cu. The total of PMe reaches higher values compared to the older generation.

3. Selected generations form geochemical zoning at the deposit. Phases of the older generation, typical by Cu and As contents, are present in the central and lower parts of the veins (Konštancia), accessible by mining works. Phases, typical by Sb and Ag contents at outskirts and upper part of veins (Konštancia, Krištof), and aggregates of younger generation are present within the frame of the open part of the vein (Konštancia) in its narrow central part.

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