SOME PECULIARITIES OF MINERALOGY OF THE DEPOSITS OF CENTRAL PART OF STRUCTURAL–METALLOGENIC ZONE SREDNA–GORA, BULGARIA

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Results of investigation of samples from the Chelopech deposit are compared with literature data. Minerals are discovered which have very similar optical features and elemental composition to fahlore, enargite and luzonite. However, their formulae are not electroneutral by calculation per 29 atoms in the unit cell or per the fahlore formula. They become electroneutral only by recalculation per larger numbers of atoms in the unit cell (32, 33 and 34 atoms). It is assumed that these are new mineral species similar in optical properties and chemical composition to fahlore, enargite and luzonite. They have following idealized formulae: $Cu^{+}_{11}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_4S_{16}$, $Cu^{+}_{11}Me^{2+}_{2}Me^{3+}\Pi Me^{3+}_{4}S_{15}$, $Cu^{+}_{10}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_4S_{16}$, $Cu^{+}_{8}Cu^{2+}_{2}Fe^{2+}_{3}As_4S_{15}$, $Cu^{+}_{8}Cu^{2+}_{3}Fe^{2+}_{2}As_4S_{15}$, $Cu^{+}_{2}Cu^{2+}_{3}As_2S_7$ (Me is the metals, ΠMe is the semimetals).
Goldfieldite and Te-tetrahedrite containing more than 24 wt.% tellurium are commonly heterogenous. They contain very small segregations of native tellurium. Moreover, tellurium may enter the sulfur position in their structure.
8 tables, 10 references.
Keywords: fahlore, enargite, luzonite, isomorphism, deposits Chelopech, Radka, Elshitsa.

The copper-pyrite deposits of Chelopech, Radka and Elshitsa are located in the central part of the Sredna-Gora structural-metallogenic zone in the ore region of Panagyurishte. This zone is characterized by the presence of copper- and iron-ore deposits of different genetic types, connected with Late Cretaceous volcanism and Laramide (Upper Cretaceous) intrusions. Copper mineralization is typical for the ore region of Panagyurishte. Two morphogenetic types of deposits are distinguished: copper-porphyritic and copper-pyrite. The Chelopech, Radka and Elshitsa deposits are of the copper-pyrite type. Ore lodes of pyrite composition (Elshitsa deposit), copper-pyrite and polymetallic copper-pyrite compositions (Chelopech and Radka deposits) are distinguished. The deposits were formed in the Late Cretaceous, associated with andesitic dacitic volcanism. They belong to the volcano-hydrothermal type (Bogdanov, 1984). Ore bodies of band-like and stock-like form are steeply dipping and are related to two subparallel volcanic zones striking north-west. They are related to dacitic or andesitic agglomerate tuffs or to contacts of these tuffs with dike-like bodies of rhyodacite. Ore bodies formed in two stages: pyrite (iron pyrite) related to dacitic volcanism, and polymetallic copper-pyrite related to subvolcanic rhyodacite.

According to V.A. Kovalenker *et al.* (1986), the following mineral paragenesises (zones in order of formation) may be distinguished at the Chelopech deposit: chalcopyrite-tennantite-pyrite, chalcopyrite-tennantite, luzonite-enargite-pyrite, and bornite-pyrite. At the Radka deposit, the first zone is eroded and the second and the third zones are exhausted. Only the first zone has been investigated at the Elshitsa deposit. About 50 hypogenic ore minerals were discovered in these deposits (Table 1). Among them there are the rare germanium minerals: briartite $Cu_8(Fe,Zn)_4Ge_4S_{16}$, germanite $Cu^{+}_{10}Me^{2+}_{3,0}Fe^{3+}_{1,0}Ge^{4+}_{2,0}As^{5+}_{1,0}S_{16}$, renierite $Cu^{+}_{10}ZnFe^{3+}_{4}Ge_2S_{16}$, the arsenic analogue of renierite $Cu_{10}Fe_4As_2S_{16}$, and $Cu_{11}Fe_4GeAsS_{16}$. According to L.R. Bernstein (1986), the latter is the end member of the renieritic solid-solution $Cu^{+}_{10}ZnFe^{3+}_{4}Ge_2S_{16} - Cu^{+}_{11}Fe^{3+}_{4}Ge^{4+}As^{5+}S_{16}$. S.N. Nenasheva ($2003_2$) named this mineral "renierite II" $Cu^{+}_{11}Fe^{3+}_{4}Ge^{4+}As^{5+}S_{16}$. Moreover, she assumed that there are three germanites (not one): germanite I $Cu^{+}_{8}Me^{2+}_{3,5}Fe^{3+}_{1.5}Ge^{4+}_{2.5}As^{5+}_{0.5}S_{16}$, germanite II $Cu^{+}_{10}Me^{2+}_{3.0}Fe^{3+}_{1.0}Ge^{4+}_{2.0}As^{5+}_{1.0}S_{16}$ and germanite III $Cu^{+}_{11.0}Me^{2+}_{3.0}Fe^{3+}_{1.0}Ge^{4+}_{3.0}S_{16}$ (Nenasheva, 2003_1). Fahlores of these deposits have their own particular features. Kovalenker *et al.* (1986) presented 50 analyses of fahlores. However, their recalculation showed that formulae from several analyses are non-electroneutral when recalculated per 29 atoms in the unit cell. A formula is considered electroneutral when its balance of valences ($\pm\Delta$ = absolute value of deviation from zero) does not exceed 3%. Formulae from several analyses become electroneutral only when they are recalculated to 32,

Table 1. **Ore minerals of the Radka, Chelopech and Elshitsa deposits by V.A. Kovalenker *et al.* (1986)**

№	Mineral	Deposit			№	Mineral	Deposit		
		Radka	Chelopech	Elshitsa			Radka	Chelopech	Elshitsa
1	Aikinite		+*		25	Marcasite	+	+	+
2	Altaite		+	+*	26	Molibdenite	+*		
3	Arsenosulvanite	+*	+*		27	Mawsonite		+*	
4	Beegerite	+*			28	Nagyagite		+	
5	Betikhtinite	+	+	+	29	Nekrasovite		+*	
6	Bornite	+	+	+	30	Pyrite	+	+	+
7	Briartite	+			31	Renierite	+	+	
8	Vinciennite	+*			32	$Cu^{+}_{10}Fe^{3+}_{4}As^{5+}_{2}S_{16}$	+*		
9	Bismuthine		+		33	$Cu^{+}_{11}Fe^{3+}_{4}Ge^{4+}As^{5+}S_{16}$	+*		
10	Wittichenite	+*	+		34	Rocesite	+*		
11	Galenite	+	+	+	35	Sylvanite		+	+
12	Gallite	+	+		36	Stannite	+	+	
13	Germanite	+			37	Sphalerite	+	+	+
14	Goldfieldite		+*	+*	38	Native tellurium		+	+*
15	Digenite	+	+		39	Tellurobismuthite		+	+
16	Native gold	+	+	+	40	Tennantite	+	+	+
17	Idaite	+	+		41	Tetradymite	+	+	+
18	Cassiterite			+	42	Tetrahedrite	+*	+	
19	Clausthalite		+*		43	Famatinite		+	
20	Covelline	+	+	+	44	Chalcosine	+	+	+
21	Coloradoite		+*		45	Chalcopyrite	+	+	+
22	Colusite	+	+		46	Hemusite		+	
23	Kostovite		+		47	Eucairite		+	
24	Luzonite		+		48	Enargite	+	+	+

Note. + — Minerals firstly discovered at these deposits by V.A. Kovalenker with co-authors (1986). + — Minerals occurring in the ores of these deposits*

Table 2. **Recalculation of fahlore analyses from the Radka, Chelopech and Elshitsa deposits (Kovalenker *et al.*, 1986) to formulae containing different amounts of atoms in the unit cell**

	Radka					Chelopech				Elshitsa		
Association, zone	Number of an. overall	Number of analyses recalculated to 29, 32, 33, 34 atoms				Number of an. overall	Number of analyses recalculated to 29, 32, 33 atoms			Number of an. overall	Number of analyses recalculated to 29 and 33 atoms	
		29	32	33	34		29	32	33		29	33
Bornite-pyrite	15	11	2	1	1	3	2		1	Analyses are abcent. Zone has not been studed		
Luzonite-enargite-pyrite	Analyses are abcent. Zone is exhausted					6	2	2	2	Analyses are abcent. Zone has not been studed		
Chalcopyrite-tennantite	Analyses are abcent. Zone is exhausted					2	2			Analyses are abcent. Zone has not been studed		
Chalcopyrite-tennantite-pyrite	Analyses are abcent. Zone is eroded					7	4	1	2	17	15	2

Note. Depth of zones increases from chacopyrite-tennantite-pyrite to bornite-pyrite zone

33 or 34 atoms in the unit cell (Tables 2, 4—6). It is likely that these are new mineral species. The foregoing induced the author to further investigate fahlores and germanium mineralization from the Chelopech deposit.

Minerals from the Chelopech deposit

Three samples from the luzonite—enargite—pyrite zone (Ch-1, Ch-992, Ch-998) were given to the author by L.A. Pautov, A.A. Agakhanov and V.Yu. Karpenko. Ten microprobe analyses were done (Table 3) using a JEOL JXA-50A electron microprobe equipped with a TRACOR—Xr energy-dispersive spectrometer at a voltage of 20 kV and current of $30x10^{-9}$ nA (analysts L.A. Pautov and A.A. Agakhanov). Calculation of concentrations was done using a ZAF-correction routine. The following standards (analytical lines) were used: ZnS ($Zn_{K\alpha}$ and $S_{K\alpha}$), GaAs ($As_{K\alpha}$), $CuFeSnS_4$ ($Cu_{K\alpha}$, $Fe_{K\alpha}$), synthetic Sb_2S_3 ($Sb_{K\alpha}$).

As a result of the investigation, the following minerals were identified:

1) Enargite (Table 3, analyses Ch-1-1, Ch-992-5, Ch-998-2). In reflected light, it is grayish-blue with very weak double reflection and strong anisotropy (color changes from dark reddish-brown to greenish-yellow). There is no cleavage or twinning. Analyses were recalculated to 8 atoms in the unit cell. $Cu^+Cu^{2+}_2AsS_4$ is idealized formula.

2) Luzonite (Table 3, analyses Ch-1-2, Ch-992-4). In reflected light, the mineral is light-gray to lilac with very weak double reflection and strong anisotropy (color changes from brown-red to green). Polysynthetic twinning is common. Analyses were recalculated to 8 atoms in the unit cell. $Cu^+Cu^{2+}_2AsS_4$ is idealized formula.

3) Tennantite is the blue and isotropic phase (Table 3, analysis Ch-998-1), occurring in association with bornite, chalcopyrite, pyrite and enargite. Recalculation to 29 atoms in the unit cell gives $Cu^+_{10.77}(Fe^{2+}_{0.70}Zn_{0.74})_{1.44}As_{4.07}S_{12.73}$ or $Cu^+_{10.8}(Fe^{2+}, Zn)_{1.4}As_{4.1}S_{12.7}$.

4) An additional phase occurs in association with enargite and luzonite, and has similar optical properties. Three analyses (Table 3, analyses Ch-1-3, Ch-1-4, Ch-1-5) were recalculated to 14 atoms in the unit cell. The average analysis gives $Cu^+_{2.00}Cu^{2+}_{3.13}Fe^{2+}_{0.09}As_{1.83}S_{6.95}$. $Cu^+_2Cu^{2+}_3As_2S_7$ is the ideal formula. We could not obtain an X-ray diffractogram of the mineral because of its intimate intergrowth with enargite and luzonite and of their similar optical characteristics.

5) A bluish isotropic phase (Table 3, analysis Ch-992-1) recalculated to $Cu^+_{8.00}Cu^{2+}_{3.00}Fe^{2+}_{2.00}(As_{4.06}Sb_{0.10})^{3+}_{4.16}S_{14.84}$ with 33 atoms in the unit cell. $Cu^+_8Cu^{2+}_3Fe^{2+}_2As_4S_{15}$ is idealized formula.

6) A grayish-bluish isotropic phase (Table 3, analysis Ch-992-2) was recalculated to $Cu^+_{8.00}Cu^{2+}_{2.44}(Zn_{0.53}Fe^{2+}_{2.23})_{2.76}(As_{3.81}Sb_{0.18})^{3+}_{3.99}S_{15.20}$ with 32 atoms in the unit cell. $Cu^+_8Cu^{2+}_2Fe^{2+}_3As_4S_{15}$ is idealized formula. According to their compositions, phases Ch-992-1 and Ch-992-2 may be the same $Cu^+_8(Cu^{2+},Fe^{2+})_5As_4S_{15}$ composition, but they occur close to each other with a definite boundary between them. Unfortunately, the segregations of the mineral are very small, and we cannot measure its X-ray diffraction pattern.

Phases Ch-992-1 and Ch-992-2 are optically similar to each other and to tennantite.

So, in addition to the minerals established by optical characterization and microprobe analysis: enargite, luzonite, tennantite, pyrite, chalcopyrite, and bornite (analyses of the last three are usual, and are not presented), we obtained analyses of three other phases of the following compositions: $Cu^+_2Cu^{2+}_3As_2S_7$, $Cu^+_8Cu^{2+}_3Fe^{2+}_2As_4S_{15}$, $Cu^+_8Cu^{2+}_2Fe^{2+}_3As_4S_{15}$, all of which are similar to each other (and to fahlore) in optical properties.

Kovalenker *et al.* (1986) presented 18 analyses of fahlores from the Chelopech deposit. Their recalculation to 29 atoms in the unit cell showed that among the fahlores of the chalcopyrite—tennantite—pyrite zone, 4 analyses (Table 4, analyses 3, 4, 5, 9) gave electroneutral formulae. Formulae for analyses 1 and 2 (Table 4) became electroneutral on recalculation to 33 atoms in the unit cell if some tellurium is considered to enter the sulfur position. Analysis 7 (Table 4) was recalculated to a formula with 32 atoms in the unit cell. It is necessary to note that, during recalculation of analyses 1 and 2 (Table 4) to a formula with 33 atoms in the unit cell, tellurium was assigned not only as Te^{4+} at the ΠMe (semimetal) position, but also as Te^{2-} in the S position. The basis for this is the fact that the amount of atoms at the ΠMe position significantly exceeds 4, and the amount of S is low compared to the formulae of complex sulfides of germanium (which are presumably analogues of these antimony-arsenic minerals). Such distribution of tellurium to different positions does not contradict the crystal-chemical features of tellurium. Minerals containing Te^{2-} at sulfur positions (for example, kervelleite $Ag^+_4Te^{2-}S$, aleksite $PbBi_2(Te_2S_2)_{\Sigma 4}$, sedlebakite $Pb_2Bi_2Te_2S_3$, and poubaite $Pb_3Bi_6(Te_4Se_6S_2)_{\Sigma 12}$ and minerals containing tellurium at both cation and anion positions (for example, nagyagite-(Te^{4+}) $Au_{2,5+x}Pb_{22+y}Te^{4+}_6\square_2(S,Te^{2-})_{35,25+0,5x+y}$; (Godovikov, 1997,

Table 3. **Recalculation of analyses of samples from the Chelopech deposit**

№ analysis of mineral phase		Cu	Fe	Zn	As	Sb	S	∑	Mineral
Ch-1-1	wt.%	47.43	0.36	–	18.63	–	32.31	98.72	Enargite
	apfu	2.97	0.03	–	0.99	–	4.01	8.00	
Ch-1-2	wt.%	49.16	0.76	–	20.39	–	33.60	103.92	Luzonite
	apfu	2.94	0.05	–	1.03	–	3.98	8.00	
Ch-1-3	wt.%	47.67	0.46	–	20.03	–	31.84	100	?
	apfu	5.20	0.06	–	1.85	–	6.89	14.00	
Ch-1-4	wt.%	47.14	0.91	–	19.47	–	32.52	100.04	?
	apfu	5.11	0.11	–	1.79	–	6.99	14.00	
Ch-1-5	wt.%	46.82	0.85	–	19.99	–	32.34	100	?
	apfu	5.09	0.10	–	1.84	–	6.96	13.99	
Average from three	wt.%	47.21	0.74		19.83		32.23	100.01	?
preceding analyses	apfu	5.13	0.09		1.83		6.95	14.00	
Ch-992-1	wt.%	43.57	6.94	–	18.95	0.76	29.66	99.88	Bluish,
	apfu	11.00	2.00	–	4.06	0.10	14.84	32.00	isotropic
Ch-992-2	wt.%	41.48	7.79	0.53	17.89	1.38	30.46	99.51	?
	apfu	10.44	2.23	0.13	3.81	0.18	15.20	31.99	
Ch-992-3	wt.%	38.16	10.88	–	17.50	0.83	32.91	100.28	?
	apfu	9.32	3.02	–	3.62	0.11	15.93	32.00	
Ch-992-4	wt.%	47.80	1.48	–	18.36	1.49	32.38	101.52	Luzonite
	apfu	2.94	0.10	–	0.96	0.05	3.95	8.00	
Ch-992-5	wt.%	46.34	2.21	0.46	19.92	–	32.37	101.31	Enargite
	apfu	2.84	0.15	0.03	1.04	–	3.94	8.00	
Ch-998-1	wt.%	46.25	2.62	3.25	20.60	–	27.57	100.29	Tennantite
	apfu	10.77	0.70	0.74	4.07	–	12.73	29.01	
Ch-998-2	wt.%	46.09	0.51	0.46	18.45	–	31.59	97.09	Enargite
	apfu	2.94	0.04	0.03	1.00	–	4.00	8.01	

№ analysis of mineral phase	Formula	Balance of valences, Δ	Δ, %
Ch-1-1	$Cu^{+}Cu^{2+}_{1.97}Fe^{2+}_{0.03}As_{0.99}S_{4.01}$	+7.97 - 8.02 = -0.05	0.6
Ch-1-2	$Cu^{+}Cu^{2+}_{1.94}Fe^{2+}_{0.05}As_{1.03}S_{3.98}$	+8.07 - 7.96 = +0.11	1.4
Ch-1-3	$Cu^{+}_{2}Cu^{2+}_{3.20}Fe^{2+}_{0.06}As_{1.85}S_{6.89}$	+14.07 - 13.78 = +0.29	2.0
Ch-1-4	$Cu^{+}_{2}Cu^{2+}_{3.11}Fe^{2+}_{0.11}As_{1.79}S_{6.99}$	+13.81 - 13.98 = -0.17	1.2
Ch-1-5	$Cu^{+}_{2}Cu^{2+}_{3.09}Fe^{2+}_{0.10}As_{1.84}S_{6.96}$	+13.90 - 13.92= -0.02	0.1
Average from three preceding analyses	$Cu^{+}_{2}Cu^{2+}_{3.13}Fe^{2+}_{0.09}As_{1.83}S_{6.95}$	+13.93 - 13.9 = +0.03	0.2
Ch-992-1	$Cu^{+}_{8.00}Cu^{2+}_{3.00}Fe^{2+}_{2.00}(As_{4.06}Sb_{0.10})^{3+}_{4.16}S_{14.84}$	+30.48 - 29.68 = +0.80	2.6
Ch-992-2	$Cu^{+}_{8.00}Cu^{2+}_{2.44}(Zn_{0.53}Fe^{2+}_{2.23})_{2.76}(As_{3.81}Sb_{0.18})^{3+}_{3.99}S_{15.20}$	+30.37 - 30.40 = -0.03	0.1
Ch-992-3	$Cu^{+}_{8.00}Cu^{2+}_{1.32}Fe^{3+}_{3.02}(As_{3.62}Sb_{0.11})^{3+}_{3.73}S_{15.93}$	+30.89 - 31.86 = -0.97	3.0
Ch-992-4	$Cu^{+}Cu^{2+}_{1.94}Fe^{2+}_{0.10}(As_{0.96}Sb_{0.05})_{1.01}S_{3.95}$	+8.11 - 7.90 = +0.21	2.6
Ch-992-5	$Cu^{+}Cu^{2+}_{1.84}(Fe^{2+}_{0.15}Zn_{0.03})_{0.18}As_{1.04}S_{3.94}$	+8.16 - 7.88 = +0.28	3.4
Ch-998-1	$Cu^{+}_{10.77}(Fe^{2+}_{0.70}Zn_{0.74})_{1.44}As_{4.07}S_{12.73}$	+25.86 - 25.46 = +0.40	1.5
Ch-998-2	$Cu^{+}Cu^{2+}_{1.94}Fe^{2+}_{0.04}Zn_{0.03}As_{1.00}S_{4.00}$	+8.02 - 8.00 = +0.02	0.0

Note. apfu – atoms per formula unit.

Table 4. **Recalculation of fahlore analyses from the Chelopech deposit given by V.A. Kovalenker *et al.* (1986)**

Zone	№	Cu	Fe	Zn	Sb	As	Te	Bi	Se	S	∑
Chp-ten-py	1	39.64	4.06	n.d.	2.01	2.48	26.16	0.34	n.d.	24.79	99.48
	2	40.30	3.87	n.d.	1.45	4.29	24.38	0.21	n.d.	24.90	99.40
	3	43.19	0.41	n.d.	7.50	2.73	17.64	n.d.	1.89	24.91	99.27
	4	45.34	0.51	0.45	2.26	6.42	17.64	0.69	0.19	25.82	99.32
	5	43.67	1.35	5.59	1.95	17.38	1.81	n.d.	n.d.	27.49	99.24
	7	42.08	1.98	6.19	4.52	16.79	n.d.	n.d.	n.d.	29.26	100.82
	9	42.73	1.83	6.21	3.98	17.81	n.d.	n.d.	n.d.	28.52	101.08
Chp-ten	17	42.79	4.87	1.51	9.15	13.87	n.d.	0.53	n.d.	27.67	100.30
	18	42.15	4.66	1.66	11.42	12.14	n.d.	0.44	n.d.	27.56	100.03
Lu-en-py	6	45.18	3.53	0.30	0.43	15.03	n.d.	7.30	0.11	27.40	99.28
	8	47.82	2.83	n.d.	1.77	17.63	n.d.	n.d.	1.74	28.43	100.22
	10	47.90	3.10	0.32	2.16	18.30	n.d.	0,17	0.23	27.94	100.12
	11	47.16	3.70	0.41	0.39	18.79	n.d.	0.64	0.20	29.44	100.73
	12	47.46	3.22	0.32	0.42	18.98	n.d.	n.d.	0.26	28.57	99.23
	13	46.58	3.08	0.11	3.19	19.03	n.d.	n.d.	1.02	27.47	100.48
Bn-py	14	48.04	2.28	1.36	0.47	20.27	n.d.	n.d.	n.d.	29.65	102.07
	15	44.23	3.55	2.30	2.19	17.92	n.d.	1.61	n.d.	28.15	99.95
	16	48.71	1.89	1.04	1.08	20.08	n.d.	n.d.	n.d.	28.54	101.34

Zone	№	n	Formula	Δ, %
Chp-ten-py	1	33	$Cu^{+}_{10}(Cu^{2+}_{1.93}Fe_{1.39})_{3.32}(Sb_{0.32}As_{0.63}Bi_{0.03}Te^{4+}_{3.02})_{4.00}(S_{14.78}Te^{2-}_{0.9})_{15.68}$	0.9
	2	33	$Cu^{+}_{10}(Cu^{2+}_{2.02}Fe_{1.31})_{3.33}(Sb_{0.22}As_{1.08}Bi_{0.02}Te^{4+}_{2.68})_{4.00}(S_{14.72}Te^{2-}_{0.94})_{15.66}$	0.0
	3	29	$Cu^{+}_{10}(Cu^{2+}_{1.43}Fe_{0.12})_{1.55}(Sb_{1.04}As_{0.61}Te^{4+}_{2.32})_{3.97}(S_{13.07}Se_{0.40})_{13.47}$	1.4
	4	29	$Cu^{+}_{11.60}(Fe_{0.15}Zn_{0.11})_{0.26}(Sb_{0.30}As_{1.39}Bi_{0.05}Te^{4+}_{2.25})_{3.99}(S_{13.10}Se_{0.04})_{13.14}$	0.2
	5	29	$Cu^{+}_{10}(Cu^{2+}_{0.40}Fe_{0.35}Zn_{1.29})_{2.05}(Sb_{0.24}As_{3.51}Te^{4+}_{0.21})_{3.96}S_{12.97}$	1.0
	7	32	$Cu^{+}_{8}Cu^{2+}_{2.80}(Zn_{1.54}Fe^{2+}_{0.52})_{2.06}(Sb_{0.60}As_{3.65})_{4.25}S_{14.88}$	2.3
	9	29	$Cu^{+}_{9.96}(Fe_{0.48}Zn_{1.41})_{1.89}(Sb_{0.46}As_{3.52})_{3.98}S_{13.17}$	2.5
Chp-ten	17	29	$Cu^{+}_{10}(Cu^{2+}_{0.23}Fe_{1.32}Zn_{0.35})_{1.90}(Sb_{1.14}As_{2.81}Bi_{0.04})_{3.99}S_{13.11}$	1.7
	18	29	$Cu^{+}_{10}(Cu^{2+}_{0.18}Fe_{1.28}Zn_{0.39})_{1.85}(Sb_{1.44}As_{2.49}Bi_{0.03})_{3.96}S_{13.19}$	3.0
Lu-en-py	6	33	$Cu^{+}_{11}(Cu^{2+}_{1.52}Fe_{0.11}Zn_{0.08})_{1.71}Fe^{3+}_{1.00}(Sb_{0.06}As_{3.53}Bi_{0.62})_{4.21}(S_{15.05}Se_{0.02})_{15.07}$	0.2
	8	32	$Cu^{+}_{8}Cu^{2+}_{3}(Cu^{2+}_{1.28}Fe_{0.83})_{2.11}(Sb_{0.24}As_{3.84})_{4.08}(S_{14.46}Se_{0.36})_{14.82}$	2.8
	10	29	$Cu^{+}_{10}(Cu^{2+}_{1.20}Fe_{0.82}Zn_{0.07})_{2.09}(Sb_{0.26}As_{3.63}Bi_{0.01})_{3.90}(S_{12.95}Se_{0.04})_{12.99}$	0.4
	11	32	$Cu^{+}_{8}Cu^{2+}_{3}(Cu^{2+}_{0.92}Fe_{1.06}Zn_{0.10})_{2.08}(Sb_{0.05}As_{4.03}Bi_{0.05})_{4.13}(S_{14.75}Se_{0.04})_{14.79}$	3.2
	12	33	$Cu^{+}_{11}(Cu^{2+}_{1.57}Fe_{0.35}Zn_{0.08})_{2.00}Fe^{3+}_{0.62}(Sb_{0.06}As_{4.26})_{4.32}(S_{15.00}Se_{0.06})_{15.06}$	1.0
	13	29	$Cu^{+}_{10}(Cu^{2+}_{0.96}Fe_{0.82}Zn_{0.02})_{1.80}(Sb_{0.39}As_{3.80})_{4.19}(S_{12.81}Se_{0.19})_{13.00}$	0.6
Bn-py	14	33	$Cu^{+}_{11}(Cu^{2+}_{1.37}Zn_{0.34})_{1.71}Fe_{0.67}(Sb_{0.06}As_{4.43})_{4.49}S_{15.13}$	1.2
	15	29	$Cu^{+}_{10}(Cu^{2+}_{0.42}Fe_{0.95}Zn_{0.53})_{1.90}(Sb_{0.27}As_{3.58}Bi_{0.12})_{3.97}S_{13.14}$	2.2
	16	29	$Cu^{+}_{10}(Cu^{2+}_{1.21}Fe_{0.49}Zn_{0.23})_{1.93}(Sb_{0.13}As_{3.92})_{4.05}S_{13.02}$	0.1

Note. Here and in the Tables 5 and 6 numbering of analyses is saved as in the work of V.A. Kovalenker with co-authors (1986); n – number of atoms in the unit cell; chp – chalcopyrite, ten – tennantite, py – pyrite, bn – bornite, lu – luzonite, en – enargite; n.d. – not detected

Godovikov and Nenasheva, 2007) are well-known in mineralogy.

Two analyses of fahlores from the chalcopyrite – tennantite zone (Table 4, analyses 17, 18) and two analyses from the luzonite – enargite – pyrite zone (Table 4, analyses 10 and 13) were recalculated to formulae with 29 atoms in the unit cell. Analyses 8 and 11 (Table 4) were recalculated to formulae with 32 atoms in the unit cell. This formula is close to the formula $Cu^{+}_{8}Cu^{2+}_{3}Fe^{2+}_{2}As^{3+}_{4}S_{15}$. Analyses 6 and 12 (Table 4) were recalculated to formulae with 33 atoms in the unit cell, close to the composition $Cu^{+}_{11}Me^{2+}_{2}Fe^{3+}As^{3+}_{4}S_{15}$. Analysis 14 (Table 4) of the mineral from the bornite – pyrite zone recalculates to this formula. Formulae for analyses 15 and 16 (Table 4), belonging to minerals from the same zone, are electroneutral on recalculation to 29 atoms per unit cell.

Fahlores of the Radka and Elshitsa deposits

At the Radka deposit, fahlores occur in three associations (tetrahedrite – tennantite, betekhtinite – bornite – sphalerite – galenite, and renierite – sphalerite – gallite) in ore bodies corresponding to the zone of bornite – pyrite ores at deep horizons of the Chelopech deposit. Other zones at the Chelopech deposit are eroded, or exhausted at the Radka deposit. Nine (of fifteen) analyses of fahlores (Table 5, analyses 1, 2, 5, 8, 9, 10, 13, 14, and 15) were recalculated to formulae with 29 atoms in the unit cell. Analyses 4 and 7 (Table 5) were recalculated to formulae with 32 atoms in the unit cell. Analyses 11 and 12 (Table 5) were recalculated to formulae with 33 and 34 atoms per cell, respectively. The formulae of analyses 3 and 6 (Table 5) are non-electroneutral because they have excess cations.

Seventeen analyses of fahlores from the Elshitsa deposit containing large amounts of tellurium occupy a special position. The formulae of two analyses (Table 6, analyses 14 and 15) are electroneutral on recalculation to the formula of fahlore, i.e. 29 atoms in the unit cell. Seven analyses (Table 6, analyses 1 – 6, 9) recalculate well to the formulae of goldfieldite only by excluding native tellurium in excess of four atoms of semimetals in the formula. The assumption that samples contain very fine inclusions of native tellurium is based on the statement of Kovalenker *et al.* (1986) that tennantite replaces goldfieldite as a result of native tellurium at this deposit. E.M. Spiridonov came to the same conclusion, based on investigation of fahlores from several volcanogenic deposits of Kazakhstan. He noticed that goldfieldite was replaced by tetrahedrite, native tellurium, and chalcopyrite (Spiridonov, 1987). Formulae for six analyses (Table 6, analyses 7, 8, 10 – 13) are electroneutral only after exclusion of native tellurium from the analyses and under the condition that all copper is monovalent. The assumption that all copper in Te-bearing fahlores is monovalent is based on the work of M.I. Novgorodova *et al.* (1978) who assumed that compensation of surplus charge in Te-bearing fahlores arising from the replacement $(As,Sb)^{3+} \rightarrow Te^{4+}$ occurs by vacancy formation. These vacancies are used by Cu^{+} as a path for diffusion. According to Mozgova and Tsepin (1983), a more probable explanation of surplus charge compensation in Te-bearing fahlores is connected with "depolarization at the expense of reduction of Cu^{2+} to Cu^{+} that limits the entrance of divalent metals into fahlores". As the formulae for these analyses are electroneutral under both conditions, one can conclude that all copper in these analyses is monovalent. Fahlores containing more than 24 wt.% tellurium may be recalculated to the same formula if we exclude native tellurium from the analyses. We recalculated a number of tellurium atoms which were excepted from every of analysis into wt.% Te and deducted its amount from total contents of Te. It was found that a tellurium can come into semimetals position up 18.8 to 23.13 wt.% Te, on the average 21.3 wt.%. That is only 21 wt.% Te can come into fahlores as isomorphous impurity. Fahlores isomorphically do not contain more than 21 wt.% tellurium. Formulae for the remaining analyses (Table 6, analyses 16 and 17) are electroneutral only on recalculation to 33 atoms in the unit cell.

Thus, 34 of 50 analyses of fahlore from the Chelopech, Radka and Elshitsa deposits are recalculated to formulae with 29 atoms in the unit cell (to the fahlore formula). Two analyses recalculate to non-electroneutral formulae. Fourteen analyses may be represented as electroneutral formulae with larger numbers of atoms in the unit cell (Table 7). From these analyses, five are recalculated to 32 atoms, eight to 33 atoms, and one is recalculated to 34 atoms in the unit cell. Ideal formulae for five analyses have the following formula $Cu^{+}_{8}(Cu^{2+}_{3}Me^{2+}_{2})_{5}\Pi Me^{3+}_{4}S_{15}$ (where Me is a metal, ΠMe is a semimetal), for two analyses $Cu^{+}_{10}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_{4}S_{16}$, for six analyses $Cu^{+}_{11}Me^{2+}_{2}Me^{3+}\Pi Me^{3+}_{4}S_{15}$, and for one analysis $Cu^{+}_{11}Me^{2+}_{3}(\Pi Me^{3+},Te^{4+})_{4}S_{16}$ with 34 atoms in the unit cell.

Results

Formulae of the phases from the Chelopech deposit are compared with non-electroneutral

Table 5. **Recalculation of fahlore analyses from the Radka deposit given by V.A. Kovalenker *et al.* (1986)**

Association	№	Cu	Ag	Fe	Zn	Sb	As	Te	Bi	S	Σ
Tetr-ten	1	41.06	0.70	0.57	6.15	16.26	8.65	0.22	1.35	25.99	100.95
	2	41.00	1.27	1.20	5.97	14.80	9.05	0.57	1.25	26.46	101.57
	3	44.76	0.45	9.61	6.05	11.10	10.48	0.36	0.50	25.40	99.71
	15	42.77	0.45	1.66	6.62	10.84	11.77	n.d.	0.65	26.42	101.18
Bet-bn-sph-ga	4	41.71	n.d.	1.09	7.90	2.09	16.75	n.d.	0,96	29.53	100.03
	5	42.88	0.12	0.51	8.15	2.41	17.58	n.d.	n.d.	27.75	99.40
	6	44.18	n.d.	0.30	8.52	3.00	17.61	n.d.	n.d.	26.62	100.23
	7	41.68	n.d.	1.06	8.10	1.50	18.24	n.d.	0.74	29.72	101.04
	8	43.62	n.d.	0.27	8.35	2.74	18.51	n.d.	n.d.	28.28	101.77
	9	44.47	n.d.	0.28	8.41	2.25	18.77	n.d.	n.d.	28.06	102.24
	10	43.45	n.d.	0.11	7.63	2.98	18.85	n.d.	n.d.	27.98	101.00
	11	43.63	0.14	0.60	7.88	0.80	19.33	n.d.	n.d.	29.43	101.81
	12	42.98	0.13	0.13	8.40	2.45	19.45	n.d.	n.d.	29.09	102.63
	14	43.20	0.18	0.09	8.34	1.38	19.70	n.d.	n.d.	28.47	101.36
Re-sph-gall	13	42.51	0.10	4.06	4.15	0.80	19.60	n.d.	n.d.	28.21	99.43

Association	№	n	Formula	Δ, %
Tetr-ten	1	29	$(Cu^{+}_{9.90}Ag_{0.10})_{10.00}(Cu^{2+}_{0.38}Fe_{0.16}Zn_{1.47}Cd_{0.03})_{2.04}(Sb_{2.12}As_{1.83}Te^{4+}_{0.03}Bi_{0.10}Sn_{0.03})_{4.11}S_{12.85}$	2.9
	2	29	$(Cu^{+}_{9.82}Ag_{0.18})_{10.00}(Cu^{2+}_{0.29}Fe_{0.34}Zn_{1.43}Cd_{0.02})_{2.08}(Sb_{1.90}As_{1.89}Te^{4+}_{0.07}Bi_{0.09}Sn_{0.03})_{3.98}S_{12.95}$	1.3
	3	29	$(Cu^{+}_{9.94}Ag_{0.06})_{10.00}(Cu^{2+}_{1.14}Fe_{0.17}Zn_{1.46}Cd_{0.03}Hg_{0.01})_{2.81}(Sb_{1.43}As_{2.19}Te^{4+}_{0.04}Bi_{0.04}Sn_{0.02})_{3.72}S_{12.46}$	7.0
	15	29	$(Cu^{+}_{10.37}Ag_{0.06})_{10.42}(Fe_{0.46}Zn_{1.56})_{2.02}(Sb_{1.37}As_{2.42}Bi_{0.05})_{3.84}S_{12.70}$	2.2
Bet-bn-sph-ga	4	32	$Cu^{+}_{8}Cu^{2+}_{2.70}(Zn_{1.97}Fe_{0.32})_{2.29}(Sb_{0.28}As_{3.64}Bi_{0.07})_{3.99}S_{15.01}$	0.2
	5	29	$(Cu^{+}_{9.98}Ag_{0.02})_{10.00}(Cu^{2+}_{0.16}Fe_{0.14}Zn_{1.87})_{2.17}(Sb_{0.30}As_{3.53})_{3.83}S_{13.00}$	0.6
	6	29	$Cu^{+}_{10.00}(Cu^{2+}_{0.50}Fe_{0.08}Zn_{1.97})_{2.55}(Sb_{0.37}As_{3.55})_{3.92}S_{12.53}$	6.7
	7	32	$Cu^{+}_{8.00}Cu^{2+}_{2.59}(Zn_{2.00}Fe_{0.31})_{2.31}(Sb_{0.20}As_{3.93})_{4.13}S_{14.97}$	0.8
	8	29	$Cu^{+}_{10.00}(Fe_{0.07}Zn_{1.88})_{1.95}(Sb_{0.33}As_{3.64})_{3.97}S_{12.98}$	0.2
	9	29	$Cu^{+}_{10.26}(Fe_{0.07}Zn_{1.89})_{1.96}(Sb_{0.27}As_{3.67})_{3.94}S_{12.83}$	1.3
	10	29	$Cu^{+}_{10.16}(Fe_{0.03}Zn_{1.73})_{1.76}(Sb_{0.36}As_{3.74})_{4.10}S_{12.96}$	0.1
	11	33	$(Cu^{+}_{11}Ag_{0.02})_{11.02}(Cu^{2+}_{0.32}Zn_{1.99})_{2.31}Fe^{3+}_{0.18}(Sb_{0.11}As_{4.25})_{4.36}S_{15.13}$	3.3
	12	34	$(Cu^{+}_{10.98}Ag_{0.02})_{11.00}(Cu^{2+}_{0.54}Fe^{2+}_{0.04}Zn_{2.19})_{2.77}(Sb_{0.34}As_{4.42})_{4.76}S_{15.46}$	0.3
	14	29	$(Cu^{+}_{9.99}Ag_{0.02})_{10.01}(Fe_{0.02}Zn_{1.88})_{1.90}(Sb_{0.17}As_{3.86})_{4.03}S_{13.05}$	0.8
Re-sph-gall	13	29	$(Cu^{+}_{9.93}Ag_{0.01})_{9.94}(Fe_{1.08}Zn_{0.94})_{2.02}(Sb_{0.10}As_{3.88})_{3.98}S_{13.05}$	0.7

Note. Tetr — tetrahedrite, ten — tennantite, bn — bornite, bet — betekhtinite, sph — sphalerite, ga — galenite, re — renierite, gall — gallite. Including, in analysis 1 — Cd 0.20, Sn 0.22 , in analysis 2 — Cd 0.14, Sn 0.22, in analysis 3 — Cd 0.19, Sn 0,17, Hg 0.14, in analysis 10 — Cd 0.14

formulae of fahlores given in the work of V.A. Kovalenker *et al.* (1986) and recalculated here to electroneutral formulae containing 32, 33 or 34 atoms in the unit cell (Table 8). The analysis of the phase Ch-992-1 and five analyses of fahlores (three from the Chelopech deposit and two from the Radka deposit) may be recalculated to the same electroneutral formulae with 32 atoms: $Cu^{+}_{8}(Cu^{2+}_{3}Me^{2+}_{2})_{5}ΠMe^{3+}_{4}S_{15}$ per unit cell. It is an indication that similar analyses obtained by different authors on different material are not accidental. These analyses may be of some new mineral. Two analyses of minerals from the Chelopech deposit (Table 4, analyses 1 and 2), when recalculated to formulae with 29 atoms in the unit cell have the following valence-balance values: 12.7% and 6.0%, respectively. If they are recalculated to a formula containing 33 atoms in the unit cell, $Cu^{+}_{10}Me^{2+}_{3}(Te^{4+},Sb,As)_{4}S_{16}$, that can be compared with the formula of germanite II, $Cu^{+}_{10}Me^{2+}_{3.0}(Fe^{3+}_{1.0}Ge^{4+}_{2.0}As^{5+}_{1.0})_{4}S_{16}$ (Nenasheva,

Table 6. **Recalculation of fahlore analyses from the Elshitsa deposit given by V.A. Kovalenker *et al.* (1986)**

Zone	№	Cu	Fe	Zn	Sb	As	Te	Bi	S	∑
Chp-ten-py	1	42.48	0.27	n.d.	0.23	4.05	26.44	2.62	25.68	101.77
	2	44.95	0.16	n.d.	0.27	4.32	25.85	0.47	25.43	101.45
	3	43.38	0.39	n.d.	0.23	5.30	25.74	0.10	25.55	100.69
	4	43.62	0.42	n.d.	0.31	5.33	25.64	0.31	25.69	100.32
	5	42.71	0.64	n.d.	0.15	4.75	24.52	3.38	25.25	101.40
	6	42.49	0.55	n.d.	0.38	5.66	24.38	1.38	25.51	100.35
	7	44.72	0.15	n.d.	0.20	5.23	23.97	0.17	26.43	100.87
	8	43.35	0.20	n.d.	0.39	5.04	23.75	0.23	26.13	99.09
	9	43.07	1.03	n.d.	0.16	5.26	23.01	1.30	25.71	99.74
	10	45.15	0.63	0.04	0.20	6.39	22.31	0.14	26.72	101.58
	11	43.83	0.74	n.d.	0.16	6.44	22.07	n.d.	26.14	99.38
	12	44.83	0.13	n.d.	0.36	6.84	21.26	1.49	26.51	101.42
	13	44.47	0.26	n.d.	0.18	5.47	21.24	2.96	26.52	101.40
	14	46.56	0.20	n.d.	0.14	6.84	19.83	0.27	26.35	100.19
	15	46.33	4.76	0.25	n.d.	20.11	1.39	n.d.	29.00	101.84
	16	46.07	4.56	0.26	n.d.	20.04	0.13	n.d.	29.26	100.32
	17	46.17	4.61	0.23	n.d.	20.35	0.23	0.34	30.34	102.27

Zone	№	n	Formula	$Te_{nat.}^{*}$	Δ, %
Chp-ten-py	1	29	$Cu^{+}_{11.30}Fe_{0.08}[(Sb_{0.03}As_{0.91}Bi_{0.21})_{1.13}Te^{4+}_{2.92}]_{4.05}S_{13.54}$	0.57	2.0
	2	29	$Cu^{+}_{11.74}Fe_{0.05}[(Sb_{0.04}As_{0.96}Bi_{0.04})_{1.04}Te^{4+}_{3.01}]_{4.05}S_{13.17}$	0.35	2.4
	3	29	$Cu^{+}_{11.44}Fe_{0.12}[(Sb_{0.03}As_{1.19}Bi_{0.01})_{1.23}Te^{4+}_{2.85}]_{4.08}S_{13..36}$	0.52	0.2
	4	29	$Cu^{+}_{11.44}Fe_{0.12}[(Sb_{0.06}As_{1.19}Bi_{0.02})_{1.27}Te^{4+}_{2.81}]_{4.08}S_{13.35}$	0.53	0.1
	5	29	$Cu^{+}_{11.39}Fe_{0.19}[(Sb_{0.02}As_{1.07}Bi_{0.27})_{1.36}Te^{4+}_{2.71}]_{4.07}S_{13.34}$	0.54	0.3
	6	29	$Cu^{+}_{11.30}Fe_{0.17}[(Sb_{0.05}As_{1.28}Bi_{0.11})_{1.44}Te^{4+}_{2.65}]_{4..09}S_{13.44}$	0.57	1.2
	7	29	$Cu^{+}_{11.40}Fe_{0.04}[(Sb_{0.03}As_{1.13}Bi_{0.01})_{1.17}Te^{4+}_{3.04}]_{4.21}S_{13.35}$	0.00	1.6
		29	$Cu^{+}_{11.48}Fe_{0.04}[(Sb_{0.03}As_{1.14}Bi_{0.01})_{1.18}Te^{4+}_{2.85}]_{4.03}S_{13.44}$	0.21	1.4
	8	29	$Cu^{+}_{11.25}Fe_{0.06}[(Sb_{0.05}As_{1.11}Bi_{0.02})_{1.18}Te^{4+}_{3.07}]_{4.25}S_{13.44}$	0.00	1.1
		29	$Cu^{+}_{11.35}Fe_{0.06}[(Sb_{0.05}As_{1.12}Bi_{0.02})_{1.19}Te^{4+}_{2.84}]_{4.03}S_{13.56}$	0.25	2.6
	9	29	$Cu^{+}_{11.29}Fe_{0.31}[(Sb_{0.02}As_{1.17}Bi_{0.10})_{1.29}Te^{4+}_{2.75}]_{4.04}S_{13.36}$	0.26	0.9
	10	29	$Cu^{+}_{11.33}Fe_{0.18}Zn_{0.01}[(Sb_{0.03}As_{1.36}Bi_{0.01})_{1.40}Te^{4+}_{2.79}]_{4.19}S_{13.29}$	0.00	1.8
		29	$Cu^{+}_{11.41}Fe_{0.18}Zn_{0.01}[(Sb_{0.03}As_{1.37}Bi_{0.01})_{1.41}Te^{4+}_{2.62}]_{4.03}S_{13.38}$	0.19	0.9
	11	29	$Cu^{+}_{11.24}Fe_{0.22}[(Sb_{0.02}As_{1.40})_{1.42}Te^{4+}_{2.82}]_{4.24}S_{13.29}$	0.00	2.4
		29	$Cu^{+}_{11.34}Fe_{0.22}[(Sb_{0.02}As_{1.41})_{1.43}Te^{4+}_{2.60}]_{4.03}S_{13.40}$	0.24	1.2
	12	29	$Cu^{+}_{11.35}Fe_{0.04}[(Sb_{0.05}As_{1.47}Bi_{0.11})_{1.65}Te^{4+}_{2.68}]_{4.31}S_{13.30}$	0.00	1.6
		29	$Cu^{+}_{11.47}Fe_{0.04}[(Sb_{0.05}As_{1.48}Bi_{0.12})_{1.65}Te^{4+}_{2.40}]_{4.05}S_{13.44}$	0.31	2.9
	13	29	$Cu^{+}_{11.36}Fe_{0.08}[(Sb_{0.02}As_{1.18}Bi_{0.23})_{1.43}Te^{4+}_{2.70}]_{4.13}S_{13.42}$	0.00	0.8
		29	$Cu^{+}_{11.41}Fe_{0.08}[(Sb_{0.02}As_{1.19}Bi_{0.23})_{1.44}Te^{4+}_{2.58}]_{4.02}S_{13.48}$	0.13	2.0
	14	29	$Cu^{+}_{11.76}Fe_{0.06}[(Sb_{0.02}As_{1.46}Bi_{0.02})_{1.50}Te^{4+}_{2.49}]_{3.99}S_{13.19}$	0.00	0.15
	15	29	$Cu^{+}_{10}(Cu^{2+}_{0.56}Fe_{1.23}Zn_{0.06})_{1.85}(As_{3.89}Te^{4+}_{0.16})_{4.05}S_{13.10}$	0.00	0.7
	16	33	$Cu^{+}_{11}(Cu^{2+}_{1.01}Fe_{0.35}Zn_{0.07})_{1.43}Fe^{3+}_{1.00}(As_{4.43}Te^{4+}_{0.02})_{4.45}S_{15.12}$	0.00	0.0
	17	33	$Cu^{+}_{11}(Cu^{2+}_{0.79}Fe_{0.34}Zn_{0.05})_{1.18}Fe^{3+}_{1.00}(As_{4.41}Bi_{0.03}Te^{4+}_{0.03})_{4.47}S_{15.35}$	0.00	2.9

Note. $Te_{nat.}^{*}$ *– amount of atoms of tellurium in the formula excluded from the analysis, after it analysis is recalculated. Results of recalculation are presented in the column «Formula»*

Table 7. **Comparison of the formulae of analyses of phases from different deposits that could be recalculated to 32, 33 and 34 atoms per unit cell**

№ table	№	n	Formula	Δ, %
4	8	32	$Cu^{+}_{8}Cu^{2+}_{3}(Cu^{2+}_{1.28}Fe_{0.83})_{2.11}(Sb_{0.24}As_{3.84})_{4.08}(S_{14.46}Se_{0.36})_{14.82}$	2.8
4	7	32	$Cu^{+}_{8}Cu^{2+}_{2.80}(Zn_{1.54}Fe^{2+}_{0.52})_{2.06}(Sb_{0.60}As_{3.65})_{4.25}S_{14.88}$	2.3
4	11	32	$Cu^{+}_{8}Cu^{2+}_{3}(Cu^{2+}_{0.92}Fe_{1.06}Zn_{0.10})_{2.08}(Sb_{0.05}As_{4.03}Bi_{0.05})_{4.13}(S_{14.75}Se_{0.04})_{14.79}$	3.2
5	4	32	$Cu^{+}_{8}Cu^{2+}_{2.70}(Zn_{1.97}Fe_{0.32})_{2.29}(Sb_{0.28}As_{3.64}Bi_{0.07})_{3.99}S_{15.01}$	0.2
5	7	32	$Cu^{+}_{8}Cu^{2+}_{2.59}(Zn_{2.00}Fe_{0.31})_{2.31}(Sb_{0.20}As_{3.93})_{4.13}S_{14.97}$	0.8
4	1	33	$Cu^{+}_{10}(Cu^{2+}_{1.93}Fe_{1.39})_{3.32}(Sb_{0.32}As_{0.63}Bi_{0.03}Te^{4+}_{3.02})_{4.00}(S_{14.78}Te^{2-}_{0.90})_{15.68}$	1.9
4	2	33	$Cu^{+}_{10}(Cu^{2+}_{2.02}Fe_{1.31})_{3.33}(Sb_{0.22}As_{1.08}Bi_{0.02}Te^{4+}_{2.68})_{4.00}(S_{14.72}Te^{2-}_{0.94})_{15.66}$	o.o.
4	6	33	$Cu^{+}_{11}(Cu^{2+}_{1.52}Fe_{0.11}Zn_{0.08})_{1.71}Fe^{3+}_{1.00}(Sb_{0.06}As_{3.53}Bi_{0.62})_{4.21}(S_{15.05}Se_{0.02})_{15.07}$	0.2
4	12	33	$Cu^{+}_{11}(Cu^{2+}_{1.57}Fe_{0.35}Zn_{0.08})_{2.00}Fe^{3+}_{0.62}(Sb_{0.06}As_{4.26})_{4.32}(S_{15.00}Se_{0.06})_{15.06}$	1.0
4	14	33	$Cu^{+}_{11}(Cu^{2+}_{1.37}Zn_{0.34})_{1.71}Fe^{3+}_{0.67}(Sb_{0.06}As_{4.43})_{4.49}S_{15.13}$	1.2
5	11	33	$(Cu^{+}_{11}Ag_{0.02})_{11.02}(Cu^{2+}_{0.32}Zn_{1.99})_{2.31}Fe^{3+}_{0.18}(Sb_{0.11}As_{4.25})_{4.36}S_{15.13}$	3.3
6	16	33	$Cu^{+}_{11}(Cu^{2+}_{1.01}Fe_{0.35}Zn_{0.07})_{1.43}Fe^{3+}_{1.00}(As_{4.43}Te^{4+}_{0.02})_{4.45}S_{15.12}$	0.0
6	17	33	$Cu^{+}_{11}(Cu^{2+}_{0.79}Fe_{0.34}Zn_{0.05})_{1.18}Fe^{3+}_{1.00}(As_{4.41}Bi_{0.03}Te^{4+}_{0.03})_{4.47}S_{15.35}$	2.9
5	12	34	$(Cu^{+}_{10.98}Ag_{0.02})_{11.00}(Cu^{2+}_{0.54}Fe^{2+}_{0.04}Zn_{2.19})_{2.77}(Sb_{0.34}As_{4.42})_{4.76}S_{15.46}$	0.3

Table 8. **Comparison of formulae obtained during investigation of the Chelopech deposit with non-electroneutral formulae of fahlore analyses by V.A. Kovalenker *et al.* (1986) recalculated to electroneutral formulae containing 32, 33 and 34 atoms per the unit cell**

Formula	Amount of atoms in the unit cell	Number of analyses	Minerals, mineral phases
$Cu^{+}_{8}(Cu^{2+}_{3}Me^{2+}_{2})_{5}\Pi Me^{3+}_{4}S_{15}$	32	5	Fahlores, according to V.A. Kova-
$Cu^{+}_{10}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_{4}S_{16}$	33	2	lenker with co-authors (1986)
$Cu^{+}_{11}Me^{2+}_{2}Me^{3+}\Pi Me^{3+}_{4}S_{15}$	33	6	Fahlores, according to V.A. Kova-
$Cu^{+}_{11}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_{4}S_{16}$	34	1	lenker with co-authors (1986)
$Cu^{+}_{8}(Cu^{2+}_{3}Fe^{2+}_{2})_{5}As_{4}S_{15}$	32	1	Ch-992-1
$Cu^{+}_{8}(Cu^{2+}_{2}Fe^{2+}_{3})_{5}As_{4}S_{15}$	32	1	Ch-992-2
$Cu^{+}_{2}Cu^{2+}_{3}As_{2}S_{7}$	14	3	Ch-1-3, Ch-1-4, Ch-1-5

2003_1), also containing 33 atoms in the unit cell, their valence-balance becomes 1.9% and 1.1%, respectively. These formulae are similar, and $Cu^{+}_{10}Me^{2+}_{3.0}(Te^{4+},\Pi Me^{3+})_{4}S_{16}$ is probably a tellurium analogue of germanite II. Te-bearing fahlores in polished section are very pale pink. Germanite is also pink, and it is no wonder that two analyses of the Te-bearing mineral from the Chelopech deposit recalculate to the fahlore formula. The remaining analyses that are recalculated to the formulae $Cu^{+}_{11}Me^{2+}_{2}Me^{3+}(\Pi Me^{3+})_{4}S_{15}$ (6 analyses), $Cu^{+}_{11}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_{4}S_{16}$, $Cu^{+}_{8}Cu^{2+}_{2}Fe^{2+}_{3}As_{4}S_{15}$ and $Cu^{+}_{2}Cu^{2+}_{3}As_{2}S_{7}$ (3 analyses) may be analyses of new minerals.

Conclusions

1. Minerals close in optical properties and elemental composition to fahlore, enargite and luzonite have been discovered in the deposits of the central part of the Sredna-Gora structural-metallogenous zone, Bulgaria. They have non-electroneutral formulae if recalculated to the fahlore formula (29 atoms in the unit cell). They are electroneutral only by recalculation to 32, 33 or 34 atoms in the unit cell. This suggests new mineral species optically and chemically similar to fahlore, enargite and luzonite with the following ideal formulae: $Cu^{+}_{10}Me^{2+}_{3}(Te^{4+},\Pi Me^{3+})_{4}S_{16}$, $Cu^{+}_{8}Cu^{2+}_{2}Fe^{2+}_{3}As_{4}S_{15}$, $Cu^{+}_{8}Cu^{2+}_{3}Fe^{2+}_{2}As_{4}S_{15}$, $Cu^{+}_{11}Me^{2+}_{2}Me^{3+}\Pi Me^{3+}_{4}S_{15}$, $Cu^{+}_{11}Me^{2+}_{3}(\Pi Me^{3+},Te^{4+})_{4}S_{16}$, $Cu^{+}_{2}Cu^{2+}_{3}As_{2}S_{7}$.

2. The tellurium analogue of germanite II may have been discovered — $Cu^{+}_{10}Me^{2+}_{3}(Te^{4+},Sb,As)_{4}S_{16}$.

3. Goldfieldites containing more than 24 wt.% of tellurium are commonly heterogenous. They contain native tellurium as fine admixtures. Formulae from their analyses

become electroneutral only after exclusion of native tellurium in excess of 4 atoms of semimetals in the formula, indicating that this tellurium is present as an admixture.

4. In Te-bearing fahlores (goldfieldite and Te-tetrahedrite), tellurium may enter the cation position (Te^{4+}) as well as the S position (Te^{2-}).

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