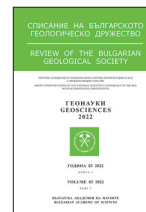




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Zonal tennantite-tetrahedrites from the Chelopech deposit: a SEM-EDS study

Зонални тенантит-тетраедрити от находище Челопеч: SEM-EDS изследване

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Abstract. The composition and structure of tennantite-tetrahedrites from blocks 17 and 18 of the copper-gold high to intermediate sulphidation Chelopech deposit were determined by SEM-EDS. Based on 31 analyses is determined that the tennantites are mostly ferrous, while the tetrahedrites are zinc-rich. In zonal tennantite-tetrahedrite aggregates, sharp saw-shape chalcopyrite bands are evidence of coupled dissolution-precipitation reactions, during the replacement of the former. The fine oscillatory zoning in other tennantite crystals also is related predominantly to internal “self-organization” processes rather than external. In some cases, however, the irregular boundaries between tennantite matrix and tetrahedrite rims and strips and their variable thickness could be due to uneven penetration of fluid into the crystal along the weak zones as a result of replacement rather than overgrowth.

Keywords: high sulphidation Cu-Au deposits, Chelopech, zonal tennantite-tetrahedrite, SEM-EDS.

Introduction

The present study reports new SEM-EDS data on the composition of tennantite-tetrahedrite minerals in the copper-gold high (to intermediate) sulphidation Chelopech deposit based on 31 analyses with integrated standards, performed with an electron microscope SEM JEOL JSM-6010 PLUS/LA and EDS detector with resolution over 129 eV MnKa at University of Mining and Geology St. I. Rilski. Heterogenous zonal aggregates of tennantite-tetrahedrite, partially or completely replacing early chalcopyrite are representative of block 18 (Fig. 1a, b, c, d, e) and less common in block 17, where replacement of tennantite by tetrahedrite is predominant (Fig. 1f, h, i). In both cases these minerals are closely associated with galena and bournonite. According to Terziev (1968), a zonal composition of pyrites at the same locality is due to a recurring weak tectonic activity that caused an unstable mineral growth with frequent fluctuations of solution saturation. The

real reasons for this morphology are probably more complex and discussed in the present paper.

Results and discussion

Figure 1a shows a zonal tennantite-tetrahedrite aggregate with slight variations in As-Sb and Fe-Zn, consisting of three rhythms divided by sharp saw-shape chalcopyrite bands. The lighter peripheral and intermediate (middle) zones are formed by Zn tetrahedrite with fine darker tennantite strips, while the core corresponds to predominantly Fe tennantite (Table 1 – analyses No 1–9). Other zonal crystals with fine compositional oscillation (Fig. 1b, c) are characterized by predominantly Fe-tennantite composition with rare tetrahedrite spots or white lines too thin to be analyzed (Table 1 – analyses No 10–15). Tennantites with lighter tetrahedrite rims (Fig. 1d, e) are more typical to block 18 (Table 1 – analyses No 16–23). In block 17, these relationships are rarely observed (Fig. 1f) because the replacement of ten-

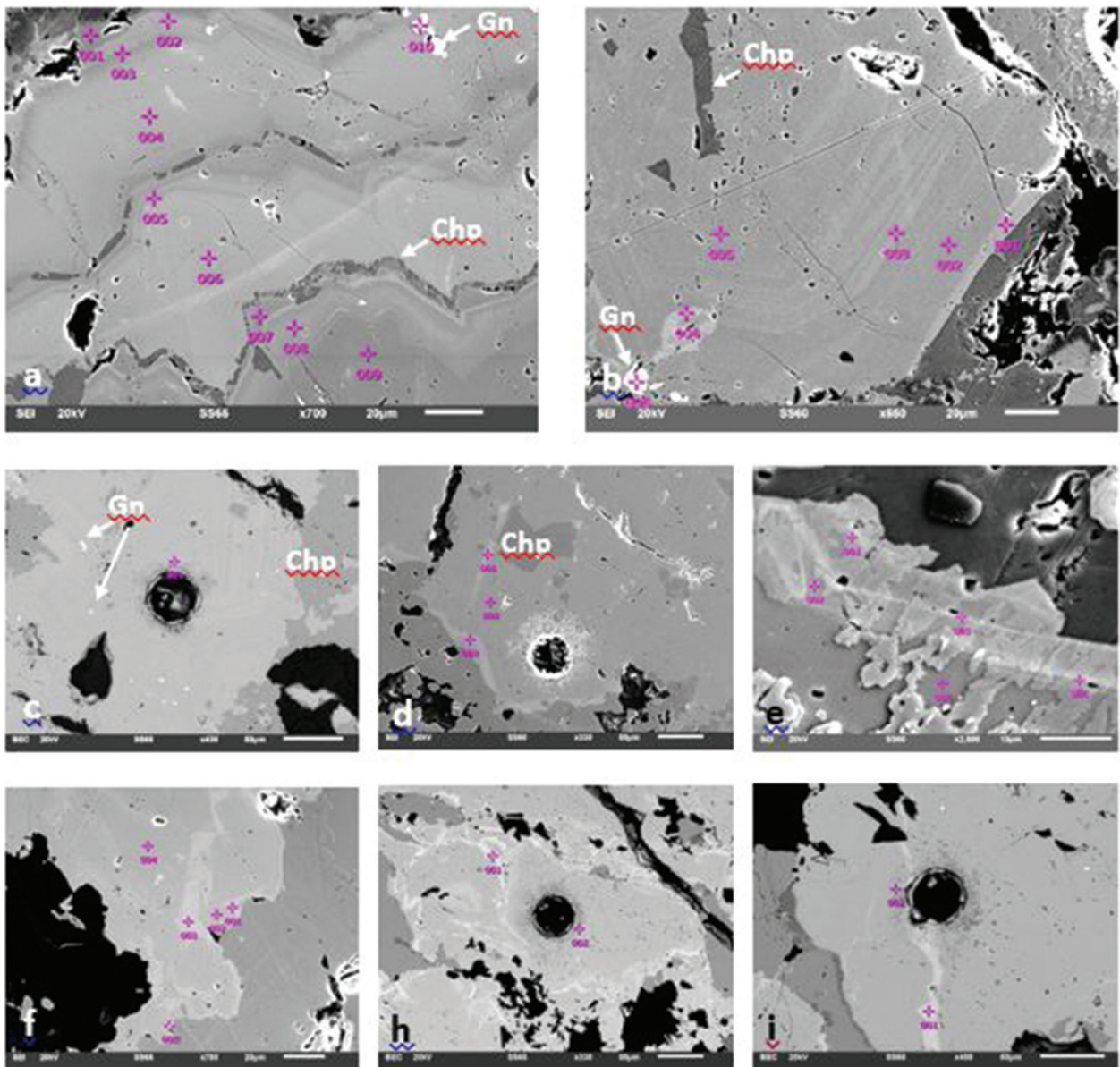


Fig. 1. SEI (Secondary Electron Image) and BSE (Backscattered Electron Image) of tennantite-tetrahedrites from the Chelopech deposit: a, b, c, d, e, sample 9b, block 18; f, h, i, sample 11, block 17. Chp, chalcopyrite; Gn, galena.

nantite by tetrahedrite is more common (Fig. 1h, i) (Table 1 – analyses No 24–31).

According to the SEM-EDS analyses in Table 1, tennantites in the deposit are mostly ferrous, while the tetrahedrites are zinc-rich. This is explained by the energetically more favorable incorporation of iron into tennantite compared to tetrahedrite (Sack, Loucks, 1985). The preferred fractionation of As and Fe into the solid phase causes a concentration gradient in the pore fluid, which stimulates the formation of zoning and heterogeneity in the newly formed aggregates (Lyubimtseva et al., 2019, 2020). The composition of the investigated tennantite-tetra-

hedrite phases is characterized by a slight metal excess and sulfur deficit but does not deviate significantly from the theoretical ones and probably due to natural heterogeneity and non-stoichiometry of sulfosalt minerals (Mozgova, Tsepin, 1983).

Sharp saw-shape chalcopyrite bands in tennantite-tetrahedrite aggregates (Fig. 1a) evidence coupled dissolution-precipitation reactions during the replacement of the former. In replacing the earlier chalcopyrite, part of the substance is redeposited as tennantite and tetrahedrite, and the residuum as chalcopyrite streaks along the edges (crystal growth walls), i.e. crystal growth occurs simultane-

Table 1. SEM-EDS analyses of tennantite-tetrahedrites (Ten-Tetr) (mass. %)*

№	Figure	EDS-point	Cu	Fe	Zn	As	Sb	S
1	1a	001	46.24	3.80	2.32	14.43	6.32	26.89
2		002	44.45	2.89	3.37	12.99	10.01	26.29
3		003	41.02	2.43	4.08	5.61	22.06	24.81
4		004	40.03	1.84	4.36	2.56	26.77	24.45
5		005	43.48	2.49	3.43	10.04	14.25	26.30
6		006	40.60	1.82	4.43	3.56	25.14	24.44
7		007	44.19	3.02	3.02	10.88	12.02	26.86
8		008	43.76	3.26	2.85	12.43	10.77	26.94
9		009	46.47	2.58	2.95	14.98	5.89	27.13
10	1b	001	43.62	3.33	3.66	12.91	10.27	26.20
11		002	47.63	2.94	2.54	18.88		28.01
12		003	46.89	2.48	2.83	14.30	6.33	27.19
13		004	41.35	1.93	4.50	5.36	21.87	24.99
14		005	48.00	2.78	3.06	17.74		28.42
15	1c	001	47.80	2.62	2.85	17.41	1.52	27.80
16	1d	001	48.05	3.73	0.80	17.78	1.51	28.14
17		002	49.14	3.11	0.83	17.91	0.89	28.11
18		003	43.91	3.43	1.03	8.13	17.88	25.61
19	1e	001	41.93	2.57	3.48	9.46	16.47	26.09
20		002	43.85	2.78	3.59	13.20	10.73	25.85
21		003	46.01	2.68	2.84	14.41	7.36	26.70
22		004	47.23	2.66	2.36	19.34	0.83	27.58
23		005	42.48	3.18	3.55	9.61	15.46	25.71
24	1f	001	42.22	2.83	4.56	5.97	18.16	26.26
25		002	46.55	3.60	3.09	17.16	1.58	28.02
26		003	40.55	1.95	4.42	7.42	20.29	25.37
27		004	46.47	3.08	2.85	18.48	0.75	28.38
28	1h	001	41.48	1.95	4.55	7.54	19.30	25.18
29		002	47.45	3.06	2.88	18.41		28.20
30	1i	001	41.48	1.97	4.49	7.22	19.54	25.28
31		002	47.23	3.17	2.85	18.95	0.51	27.30

* All analyses are normalized to 100%. Analyst: Georgy Lutov

1. Cu _{11.02} (Fe _{1.03} Zn _{0.54}) _{1.57} (As _{2.92} Sb _{0.79}) _{3.71} S _{12.70}	⇒ Fe Ten	17. Cu _{11.42} (Fe _{0.82} Zn _{0.19}) _{1.01} (As _{3.53} Sb _{0.11}) _{3.64} S _{12.94}	⇒ Fe Ten
2. Cu _{10.80} (Fe _{0.80} Zn _{0.80}) _{1.60} (As _{2.68} Sb _{1.27}) _{3.95} S _{12.66}	⇒ Fe Ten	18. Cu _{11.00} (Fe _{0.98} Zn _{0.25}) _{1.23} (Sb _{2.34} As _{1.73}) _{4.07} S _{12.71}	⇒ Fe Tetr
3. Cu _{10.51} (Zn _{1.02} Fe _{0.71}) _{1.73} (Sb _{2.95} As _{1.22}) _{4.17} S _{12.60}	⇒ Zn Tetr	19. Cu _{10.43} (Zn _{0.84} Fe _{0.73}) _{1.57} (Sb _{2.14} As _{2.00}) _{4.14} S _{12.86}	⇒ Zn Tetr-Ten
4. Cu _{10.46} (Zn _{1.11} Fe _{0.55}) _{1.66} (Sb _{3.65} As _{0.57}) _{4.22} S _{12.66}	⇒ Zn Tetr	20. Cu _{10.73} (Zn _{0.85} Fe _{0.77}) _{1.62} (As _{2.74} Sb _{1.37}) _{4.11} S _{12.53}	⇒ Zn Ten
5. Cu _{10.71} (Zn _{0.82} Fe _{0.70}) _{1.52} (As _{2.10} Sb _{1.83}) _{3.93} S _{12.84}	⇒ Zn Ten	21. Cu _{11.05} (Fe _{0.73} Zn _{0.66}) _{1.39} (As _{2.94} Sb _{0.92}) _{3.86} S _{12.70}	⇒ Fe Ten
6. Cu _{10.56} (Zn _{1.12} Fe _{0.54}) _{1.66} (Sb _{3.41} As _{0.79}) _{4.20} S _{12.59}	⇒ Zn Tetr	22. Cu _{11.04} (Fe _{0.71} Zn _{0.54}) _{1.25} (As _{3.84} Sb _{0.10}) _{3.94} S _{12.78}	⇒ Fe Ten
7. Cu _{10.74} (Fe _{0.84} Zn _{0.71}) _{1.55} (As _{2.24} Sb _{1.53}) _{3.77} S _{12.94}	⇒ Fe Ten	23. Cu _{10.56} (Fe _{0.90} Zn _{0.86}) _{1.76} (As _{2.03} Sb _{2.00}) _{4.03} S _{12.66}	⇒ Fe Ten-Tetr
8. Cu _{10.59} (Fe _{0.90} Zn _{0.67}) _{1.57} (As _{2.55} Sb _{1.36}) _{3.91} S _{12.92}	⇒ Fe Ten	24. Cu _{10.51} (Zn _{1.10} Fe _{0.80}) _{1.90} (Sb _{2.36} As _{1.26}) _{3.62} S _{12.96}	⇒ Zn Tetr
9. Cu _{11.06} (Fe _{0.70} Zn _{0.68}) _{1.38} (As _{3.03} Sb _{0.73}) _{3.76} S _{12.80}	⇒ Fe Ten	25. Cu _{10.84} (Fe _{0.95} Zn _{0.70}) _{1.65} (As _{3.39} Sb _{0.19}) _{3.58} S _{12.93}	⇒ Fe Ten
10. Cu _{10.61} (Fe _{0.92} Zn _{0.87}) _{1.79} (As _{2.66} Sb _{1.30}) _{3.96} S _{12.63}	⇒ Fe Ten	26. Cu _{10.30} (Zn _{1.09} Fe _{0.56}) _{1.65} (Sb _{2.69} As _{1.60}) _{4.29} S _{12.76}	⇒ Zn Tetr
11. Cu _{11.05} (Fe _{0.78} Zn _{0.57}) _{1.35} As _{3.72} S _{12.88}	⇒ Fe Ten	27. Cu _{10.78} (Fe _{0.81} Zn _{0.64}) _{1.45} (As _{3.64} Sb _{0.09}) _{3.73} S _{13.04}	⇒ Fe Ten
12. Cu _{11.17} (Fe _{0.67} Zn _{0.66}) _{1.33} (As _{2.89} Sb _{0.79}) _{3.68} S _{12.83}	⇒ Fe Ten	28. Cu _{10.51} (Zn _{1.12} Fe _{0.56}) _{1.68} (Sb _{2.55} As _{1.62}) _{4.17} S _{12.64}	⇒ Zn Tetr
13. Cu _{10.58} (Zn _{1.12} Fe _{0.56}) _{1.68} (Sb _{2.92} As _{1.16}) _{4.08} S _{12.66}	⇒ Zn Tetr	29. Cu _{10.99} (Fe _{0.81} Zn _{0.65}) _{1.46} As _{3.62} S _{12.94}	⇒ Fe Ten
14. Cu _{11.09} (Fe _{0.73} Zn _{0.69}) _{1.42} As _{3.48} S _{13.01}	⇒ Fe Ten	30. Cu _{10.51} (Zn _{1.11} Fe _{0.57}) _{1.68} (Sb _{2.58} As _{1.55}) _{4.13} S _{12.69}	⇒ Zn Tetr
15. Cu _{11.17} (Fe _{0.99} Zn _{0.18}) _{1.17} (As _{3.51} Sb _{0.18}) _{3.69} S _{12.97}	⇒ Fe Ten	31. Cu _{11.04} (Fe _{0.84} Zn _{0.65}) _{1.49} (As _{3.76} Sb _{0.06}) _{3.82} S _{12.65}	⇒ Fe Ten
16. Cu _{11.16} (Fe _{0.70} Zn _{0.65}) _{1.35} (As _{3.45} Sb _{0.19}) _{3.64} S _{12.86}	⇒ Fe Ten		

ously, which is confirmed by their jagged borders. When the solid layer is precipitated, it compresses the residual fluid and its physicochemical parameters change, including ion concentration, and the next band has a different composition. However,

this process to occur the tectonic setting has to be relatively non-dynamic.

So, the reasons for the rhythmic generation of this tennantite-tetrahedrite aggregate are rather internal than external. This explanation could also be

applied to the tennantites with thin, lighter Sb-rich streaks (Fig. 1b, c), i.e. oscillatory zoning in Fe-tennantite crystals in block 18 is related predominantly to “self-organization” processes (especially the appearance of a concentration gradient at the mineral-fluid boundary and kinetic phenomena on the mineral growth surface).

However, the influence of external factors caused by variation in physicochemical conditions (temperature, fS_2 , fO_2 , pH) cannot be completely excluded, especially considering the random fluctuations typical to near-surface epithermal ore deposition, including fluid boiling or mixing, and a periodic weak tectonic activity. This is confirmed by widespread substitution processes in Chelopech, including the replacement of chalcopyrite by tennantite (which would also explain the increased content of Fe in tennantite) and tennantite by tetrahedrite (Fig. 1h, i) as well as a diverse mineral composition of the blocks in the deposit.

The interpretation of the tennantite-tetrahedrite relationships in the other figures is much more ambiguous: whether it is overgrowth or replacement? Sharp boundaries and preference to growth surfaces suggest overgrowth (Fig. 1d, f). However, at a higher resolution (Fig. 1e), irregular boundaries between two mineral phases and its variable thickness could be due to uneven penetration of fluid into the crystal

along the weak zones, which in this case indicates that the rim was formed as a result of a replacement rather than overgrowth.

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