Sulfosalt mineral compositions from the No 10 vein, Zletovo lead-zinc deposit, Macedonia

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Abstract. This paper presents results obtained from electronic microprobe of analyses of sulfosalt minerals and other phases from ore vein [1] 10 at the Zletovo lead zinc deposit, Macedonia. The vein contains galena, sphalerite, pyrite, chalcopyrite, siderite, tetrahedrite-tennantite, luzonite, stibioluzonite and pearceite. The tetrahedrite-tennantite series ranges from pure tetrahedrite to pure tennantite. Pearceite and luzonite have near-ideal stochiometric compositions.

Keywords. Zletovo, sulfosalts, tetrahedrite, tennantite, luzonite, pearceite

1 Introduction

The Zletovo lead-zinc deposit is located in Macedonia. It formed during hydrothermal activity that was intimately associated with Tertiary volcanism along an active continental margin. The major rock types in the area are andesite, dacite, dacitic ignimbrite and volcanic tuff (Serafimovski 1990; Serafimovski and Alexandrov 1995; Tasev 2003). Dacitic ignimbrite is the most common volcanic unit.

Pb-Zn mineralization at Zletovo is spatially and genetically related to fracture zones that trend NW, NNW and ENE. These fractures appear to have served as the main conduits and depositional sites for hydrothermal fluids. Mineralization has infilled joints and brecciated zones, and has replaced wallrocks. The orebodies comprise numerous veins and associated stockwork mineralization in areas of altered wallrocks. Most of the veins have a strike length of more than 1 km. Ore vein No 10 is exceptional because it can be followed for up to 10 km along strike. Vein thickness ranges from a few cm up to 2m. The veins generally dip from 40° to near-vertical, averaging about 60°. The veins have been intersected at depths of up to 500 m.

The morphologies and compositions of the ore veins from Zletovo are generally similar. We use ore vein No 10 as the type example (Fig. 1). The central vein consists primarily of massive sulphide ore, and contains clay-altered clasts of volcanic rocks. Sulfides have impregnated the intensely clay-altered wallrocks adjacent to the veins. Siderite bands occur near the vein walls (Fig. 1).

The ore mineral association comprises galena as the principal ore mineral together with sphalerite and subordinate pyrite, siderite and chalcopyrite, and rare pyrrhotite, marcasite, and magnetite. Minor occurrences of U-mineralization (pitchblende) have also been discovered. Detailed information about the mineral parageneses and geochemical features of the major minerals in ore veins is provided in Mudrinic and Serafimovski (1991) and Serafimovski and Tasev (2003).

The veins typically contain large clasts or screens of altered dacitic and andesitic wallrocks. The altered clasts are weakly mineralized or barren.

2 Methodology

We have examined sulfides and sulfosalts petrographically from five samples of ore vein No. 10 (Fig. 2). Selected minerals were then analyzed for S, Fe, Co, Cu, Zn, Ge, As, Ag, Cd, In, Sn, Hg, Pb and Bi using wavelength dispersive spectrometry electron microprobe analysis using a CAMECA / CAMEBAX microprobe. The estimated precision is low for Sb, Zn, As, and Ag (1–3%, 3–10%, 10–15%, respectively) and somewhat worse for Pb, Cd, In and Sn (2–5%, 5–15%, 15–30%, respectively).

Detectable contents of Sn and In were only found in some tetrahedrites, whereas Co, Ge, Hg and Bi were always below detection limits. Detection limits for Hg and Bi, were fairly high (>0.4–0.6%), partly because of interference between different elemental X-ray spectra. Detection limits for As and Pb were also high (0.25%) compared to other elements (Fe 0.05; Co, Cu 0.07; Zn, Ag, In, Sn 0.1; Cd, Ge 0.13).

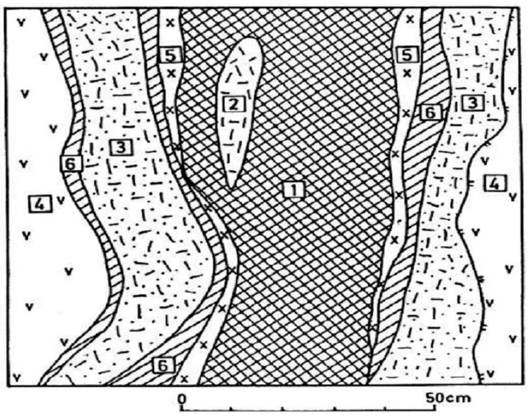

Figure 1: Schematic section through ore vein No 10, Zletovo mine. 1. Massive Pb-Zn sulfide ore; 2. Clast of Dacitic-andesitic ignimbrite (slightly kaolinized); 3. Dacitic-andesitic ignimbrite (intensely kaolinized); 4. Dacitic-andesitic ignimbrite; 5. Siderite; 6. Dacitic-andesitic ignimbrite, with galena impregnations

3 Results and discussion

Composition of pearceite, luzonite and tennantite-tetrahedrite are listed in Tables 1 and 2.

3.1 Luzonite (Cu_3AsS_4)

Luzonite was observed in samples #3 and #5. Luzonite in sample #3 is slightly more Fe-rich (0.15–0.66 %) and Sb-poor (0.17–2.5 %) relative to sample #5 (Fe?0.14 %; Sb 1.7–3.8 %). Luzonite contains minor Zn (?0.26 %), Ag (?0.17 %) and Cd (?0.15 %) in sample #3, but these elements are lower or absent in sample #5. Analysis 5-3Lu2 is close to the ideal stochiometric compositions of luzonite (Table 1).

3.2 Pearceite ($Ag_{13\text{-}11}Cu_{3\text{-}5}As_2S_{11}$)

A pearceite grain with 59 % Ag and $Sb/(Sb + As)_{mol}$ = 0.14 was analyzed from sample #5 (Table 1). Pearceite occurs as rare, small grains associated with luzonite + tennantite + galena + pyrite + chalcopyrite.

3.3 Tetrahedrite ($Cu_{12}Sb_4S_{13}$) – Tennantite ($Cu_{12}As_4S_{13}$)

Our microprobe analyses (Table 2) have revealed that Zletovo tetrahedrites are members of the tetrahedrite–tennantite solid solution [Sb/(Sb + 1%). Within individual samples, Ag is systematically higher in more Sb-rich grains or portions of composite grains and Ag decreases in areas that have more tennantitic compositions. The highest Ag contents occur in fine (a few microns diameter) droplets of tetrahedrite inside galena crystals in sample #4, which comes from a galena + sphalerite + pyrite + tetrahedrite-tennantite veinlet. These may actually represent the main Ag-bearing sites within what have previously been reported as Ag-bearing galena from Zletovo (up to 1250 ppm; $As)_{mol}$ = 0.04–0.94]. They contain significant Zn (usually 7–8 %) and Ag (from none to 5.5 %). Fe contents are always relatively low (?3%, usually Mudrinic and Petkovic 1982). Cd contents in tetrahedrite can be significant. They are typically <0.3 %, but locally can be as high as 1.1 % in some of the abovementioned droplets. A tetrahedrite droplet contains detectable In (0.15 %). Sn contents just above the detection limit (0.10–0.12 %) have been measured in more Sb-rich parts of the grains. Sample #2 has a particularly coarse grainsize, and has tetrahedrite – tennantite compositions characterized by an intermediate $Sb/(Sb + As)_{mol}$ ratio of 0.44.

Analyses of fine grained tetrahedrites may have been affected by contamination from neighboring phases. This may be the source of the locally significant Pb contents (up to 0.48%). Overall, the tetrahedrite analysis with the closest composition to ideal stochiometry is 3-5 Tet2 (Table 2).

Tennantites from Zlotovo contain significant Zn (1.72–8.33 %) and Sb (1.32-7.38%; Table 2). Fe is relatively low (0.1-3.06%). Within individual samples, the content Ag

Table 1: Results of WDS microprobe analyses of pearceite (Pea) and luzonite (Lu) from ore vein No 10, Zletovo ore deposit. All data listed as atomic %.

	5-2 Pea3	5-2 Lu3	5-2 Lu4	5-3 Lu2	3-5 Lu?	3-5 Lu?	3-1 Lu6	3-1 Lu7
S	17.41	32.04	31.84	32.62	32.29	32.55	32.87	32.68
Fe	0.03	0.05	0.14	0.01	0.53	0.66	0.15	0.19
Co	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.02
Cu	15.18	47.24	46.74	48.00	46.97	47.23	47.86	47.59
Zn	0.03	0.03	0.14	0.00	0.04	0.12	0.23	0.26
Ge	0.09	0.00	0.03	0.01	0.00	0.00	0.01	0.06
As	6.31	16.67	16.21	17.79	17.50	18.92	18.27	18.03
Ag	58.63	0.03	0.08	0.03	0.17	0.15	0.03	0.09
Cd	0.34	0.00	0.03	0.00	0.01	0.15	0.01	0.02
In	0.00	0.03	0.00	0.00	0.00	0.03	0.00	0.03
Sn	0.00	0.00	0.00	0.00	0.02	0.00	0.03	0.01
Sb	1.64	3.12	3.77	1.67	2.48	0.17	0.75	0.67
Hg	0.05	0.00	0.17	0.00	0.12	0.00	0.00	0.15
Pb	0.18	0.00	0.10	0.00	0.15	0.14	0.00	0.07
Bi	0.29	0.00	0.00	0.20	0.00	0.00	0.00	0.00
Sum	100.17	99.20	99.25	100.33	100.27	100.14	100.21	99.87

Table 2: Results of WDS microprobe analyses of tetrahedrite (Tet) and tennantite (Ten), from ore vein No 10, Zletovo ore deposit. All data listed as atomic %.

	3-4 Ten	3-1 Ten4As	5-2 Ten (2)	5-2 Ten3	3-5 Tet1	3-5 Tet2	3-4 Tet
S	27.27	28.00	28.04	28.03	25.16	26.48	26.48
Fe	0.10	0.36	0.22	3.06	0.37	0.17	0.05
Co	0.01	0.00	0.02	0.03	0.00	0.01	0.00
Cu	40.74	41.73	42.26	45.37	35.42	37.97	38.92
Zn	8.31	8.33	8.13	1.72	7.37	7.81	8.20
Ge	0.00	0.00	0.05	0.04	0.04	0.06	0.08
As	14.94	18.86	18.06	17.85	3.59	9.35	9.53
Ag	0.49	0.44	0.03	0.15	1.89	1.15	1.13
Cd	0.24	0.17	0.18	0.61	0.30	0.24	0.12
In	0.00	0.07	0.01	0.00	0.02	0.01	0.04
Sn	0.00	0.01	0.00	0.05	0.11	0.10	0.10
Sb	7.38	1.32	2.56	2.55	24.52	15.98	15.55
Hg	0.14	0.14	0.07	0.10	0.14	0.02	0.00
Pb	0.08	0.38	0.17	0.21	0.48	0.09	0.00
Bi	0.00	0.00	0.00	0.00	0.16	0.33	0.00
Sum	99.68	99.81	99.77	99.77	99.56	99.75	100.20

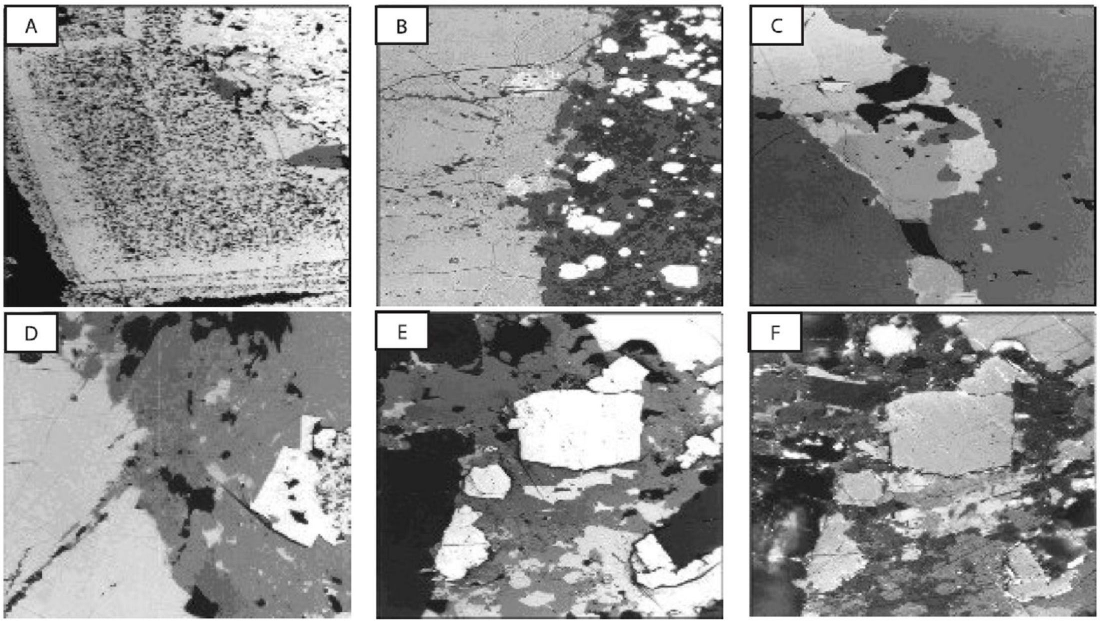

Figure 2: Photomicrographs of sulfides and sulfosalts from Zletovo (ore vein No10). A) Late generation of zoned galena with abundant quartz inclusions. An earlier generation of galena-sphalerite-pyrite-tetrahedrite ore comprises the background. B) Contact between intensively pyritized volcanic fragments and massive zoned sphalerite (gray). C) Sphalerite cut by vein composed of galena (light gray), tetrahedrite (gray), chalcopyrite (medium gray, upper part), quartz and traces of pyrite. D) Pyrite (white), chalcopyrite (light gray, left part), tenantite (gray in lower and central part) with inclusions of galena (light gray) and luzonite-stibioluzonite (dark gray, lower central part). Oil immersion. E) Complex intergrowth of pyrite crystals (white), sphalerite (dark gray), galena (white, irregular shapes), chalcopyrite (light gray, center) tennantite (middle to dark gray, central area) and luzonite-stibioluzonite (dark gray, strongly pleochroic, central part). Oil immersion. F) Partially crossed nicols. Lamellar twinning in one direction in luzonite-stibioluzonite (light to middle gray, central and lower part), and "flashy" internal reflections of tennantite (dark gray, left part).

decreases as end-member tennantite compositions are approached. Cd contents are significant in some samples, usually between 0.17 and 0.61%. Two samples contained detectable In (0.01 and 0.07%). Sn contents are just above the detection limit (0.01-0.05%).

3.4 Galena

Galena from the No. 10 vein is almost pure PbS. It locally contains significant Cu (0.7 %), Zn (<0.4 %), Fe (0.16 %) and Cd (0.16%). It is not clear whether these elements occur as fine inclusions or within the galena crystal lattice.

3.5 Sphalerite

The Zlotovo sphalerite is characterized by low Fe contents (usually ?1 %). Higher Fe contents have been detected locally in sample #3 (?6 %) and #5 (?2 %). Grain-to-grain and within-grain variations in Fe tenors show no systematic patterns. The highest Fe contents are typically associated with the lowest Cd contents, which reach 0.5–0.8 % in the least ferrous compositions. Minor amounts of Cu, Sb and Pb have been detected in some grains. Late-stage schalenblende has been detected in sample #3. It is distinctly cathodoluminescent under the electron beam and has a composition of almost pure sphalerite, with detectable As (0.3 %) and low Cd (0.15 %).

3.6 Chalcopyrite

Our analyses have shown that chalcopyrite is virtually pure $CuFeS_2$. All other elements were below detection limits.

3.7 Pyrite

Significant As contents are found in all generations of pyrite from Zlotovo. They can probably be ascribed to fine, unresolved intergrowths with arsenopyrite, as suggested by the crystal chemical formulae (S+As=Fe). Minor Cu (0.7%) has been detected in late euhedral or partially resorbed pyrite grains that occur with galena, sphalerite, tetrahedrite-tennantite and luzonite. Early pyrite grains are virtually Cu-free, except for sample #5, where an early pyrite grain contains significant Cu (0.36 %) and high As (4.4 %) contents. Detectable Pb (0.26 %) has been found in early and late-stage pyrite grains.

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4 Conclusions

Results from the latest field and laboratory studies of ore vein No. 10 in Zletovo lead-zinc mine have shown an unusual group of sulfosalt minerals associated with the massive lead-zinc sulfide vein. Galena and sphalerite are associated with tetrahedrite, tennantite, pyrite, chalcopyrite, quartz, calcite, siderite luzonite and pearceite. Results of electron microprobe analyses have shown a huge range in tetrahedrite and tennantite compositions from essentially pure tetrahedrite through to pure tennantite.

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Close