New data concerning the major ore minerals and sulphosalts from the Pb-Zn Zletovo Mine, Macedonia

Novi podatki o glavnih rudnih mineralih in sulfosoleh iz Pb-Zn rudišča Zletovo (Republika Makedonija)

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Received: May 18, 2005 **Accepted:** October 28, 2005

Abstract: Based on its mineral content (around 40 minerals) and certain solid solution mineral phases, Zletovo has been classified as a subvolcanic hydrothermal Pb-Zn ore deposit. The main ore minerals are galena and sphalerite. They occur in very characteristic structures, microstructures and textures, which often enclose sulphosalt mineral phases. The most common sulphosalts are bournonite, boulangerite, proustite and luzonite. So far the sulphosalt minerals and their solid solution phases from the Zletovo ore deposit have not been studied in detail. This paper presents the results of a detailed study of ore samples from different levels of the Zletovo mine based on electron microprobe analysis. In the already known mineral assemblage, which is composed mainly of galena, sphalerite, pyrite, chalcopyrite, and siderite, the sulphosalts series, which includes tetrahedrite-tennantite, luzonite, stibioluzonite and pearceite, was distinguished. The composition of the tetrahedrite-tennantite solid solution ranges from pure tetrahedrite to pure tennantite, with the presence of minerals that are representatives of the processes of the intermixing of solid solutions. The compositions of the determined pearceites and luzonites almost match the compositions of the standards for these minerals.

Izvleček: Glede na pestro mineralno paragenezo (okrog 40 mineralov) in določene mineralne faze uvrščamo rudišče Zletovo med subvulkanska hidrotermalna Pb-Zn rudišča. Glavna rudna minerala sta galenit in sfalerit, ki kažeta značilne strukture, mikrostrukture in teksture, značilne za hidrotermalna rudišča. Zelo pogosto ju obdajajajo minerali iz skupine sulfosoli. Najbolj pogosto gre za bournonit, boulangerit, proustit in luzonit. Do sedaj minerali sulfosoli iz rudišča Zletovo podrobno niso bili raziskani. V okviru te študije smo z detajlno raziskavo rudnih vzorcev iz različnih obzorij s pomočjo elektonskega mikroanalizatorja poleg glavnih rudnih mineralov kot so galenit, sfalerit, pirit halkopirit in siderit našli še nekatere nove minerale iz skupine sulfosoli. Gre za trde raztopine sistema tetraedrit-tenantit, mineral pearceit ter že prej poznani luzonit, ki zaenkrat še ni bil podrobneje raziskan. Sestava pearceita in luzonita se v glavnem ujema s standarno sestavo teh mineralov.

Key words: Zletovo Mine, mineral paragenesis, ore minerals, sulphosalts
Ključne besede: Rudnik Zletovo, mineralna parageneza, rudni minerali, sulfosoli

Scientific paper

INTRODUCTION

The Zletovo Pb-Zn ore deposit is situated along the active continental margin and is intimately associated with Tertiary volcanism and related hydrothermal activity. The Zletovo Mine is located in the eastern part of the Kratovo-Zletovo volcanic complex. It lies about 5 km NW of the Zletovo village and about 7 km from the town of Probištip.

The first detailed exploration was started in 1928 by the English Selection Mines Limited company and was finished in 1939 when the Zletovo deposit was prepared for exploitation with an annual capacity of 120 000 t of raw ore. Exploitation of the Zletovo Mine have began again during the Second World War with an annual capacity of 400 000 t. The mine is still active up to date and produces lead-zinc concentrates. During the long history of the exploration and exploitation of the Zletovo ore deposit several contributions concerning the origin and the genetic characteristic were published (CISSARZ AND RAKIĆ, 1956; RADUSINOVIĆ, 1961; PANTIĆ ET AL., 1973; DENKOVSKI, 1974; RAKIĆ, 1978; BLEČIĆ, 1981, 1983; PETKOVIĆ, 1982; ZARIĆ, 1982; SERAFIMOVSKI, 1990, 1993; EFREMOV, 1993; SERAFIMOVSKI AND BOEV, 1996; SERAFIMOVSKI AND TASEV, 2003).

There are also a lot of bibliographic materials and annual reports that have resulted from the exploration of the Zletovo Mine concerning the domain of the volcanic rocks, the fault structures, the mineralogical and the genetical features of the deposit. These can be found in the Zletovo Mine's library, the library of the Geoinstitute-Skopje, and in the Ministry of the Economy of the Republic of Macedonia.

GEOLOGICAL SETTING

The major lithologies in the area are related to Tertiary volcanism, and are represented by andesites, dacites, dacitic ignimbrites and volcanic tuffs (SERAFIMOVSKI, 1990; SERAFIMOVSKI AND ALEXANDROV, 1995; TASEV, 2003, etc.). Dacitic ignimbrites are the most common volcanic rocks in the mining area. Pb-Zn mineralization is spatially and genetically related to fracture and brecciated zones trending NW-SE, NNW-SSE and ENE-WSW. These structures served as conduits and/or depositional sites for ore and gangue minerals, precipitating from the circulating hydrothermal fluids. Ore also occurred as a metasomatic replacement of the wall rocks by ore minerals. Numerous veins and the associated stockwork mineralization thus represent the ore bodies; their thickness ranges from a few centimetres up to 2 m. The veins generally dip from 40° to vertical, averaging about 60°. They are usually more than 1 km long, the exception is ore vein No.10, which is more than 10 km long and reaches the area of the Plavica pollymetallic ore deposit (Fig. 1). A total of 16 ore veins have been found in the Zletovo Mine.

Some ore veins are characterized by apophyses, which are shorter and thinner than the main veins. It should be pointed out that the host rock of the ore veins is very often hydrothermally altered. The alteration is mostly represented by kaolinitization and/or silicification. The hydrothermally altered zones around the ore veins are usually barren or poorly impregnated with ore minerals. Mineral vein paragenesis is represented by galena which is the main ore mineral and sphalerite with subordinate pyrite, a lesser amount of siderite and chalcopyrite as well

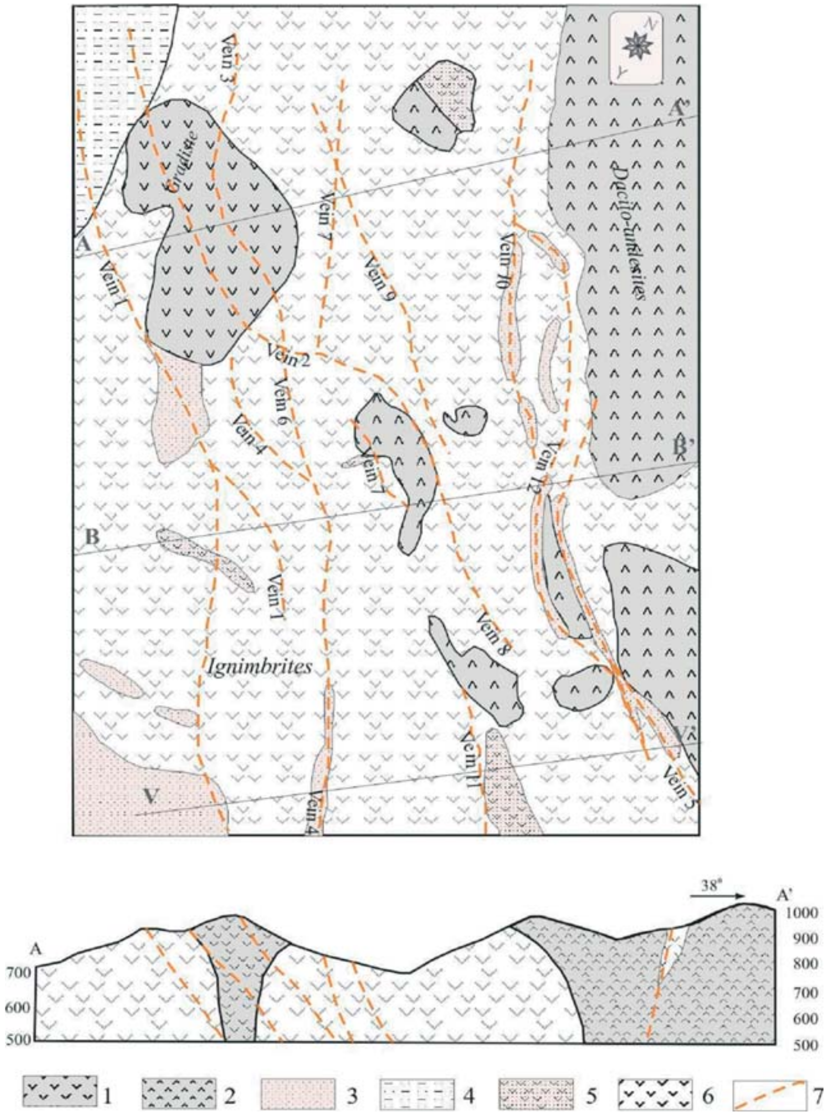


Figure 1. Geological map and cross section of the Pb-Zn Zletovo ore deposit (Serafimovski, 1990)
1) Hydrothermally altered andesite, 2) Hydrothermally altered dacite, 3) Hydrothermally altered and silicified ignimbrite, 4) Stratified tuff, 5) Hydrothermally altered dacite-andesite, 6) Ignimbrite, 7) Ore veins
Slika 1. Geološka karta in profil Pb-Zn rudišča Zletovo (Serafimovski, 1990)
1) hidrotermalno spremenjeni andezit, 2) hidrotermalno spremenjeni dacit, 3) hidrotermalno spremenjeni ignimbrit, 4) plastoviti tuf, 5) hidrotermalno spremenjeni dacit-andezit, 6) ignimbrit, 7) rudne žile

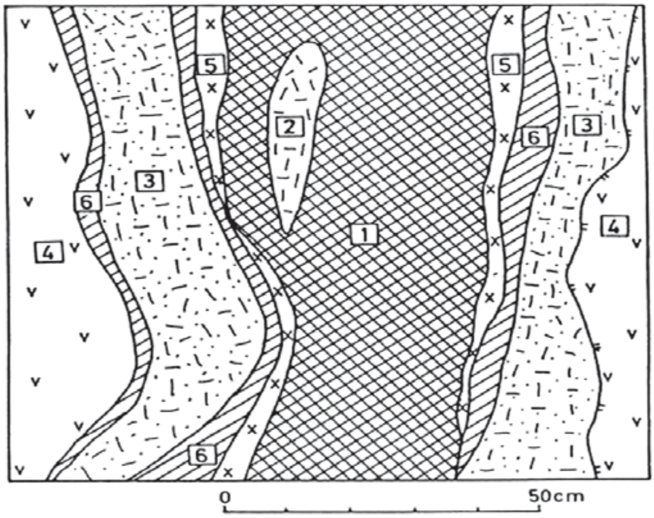


Figure 2. Detail of ore vein No. 10, Zletovo ore deposit
1) Pb-Zn ore, 2) Dacito-andesitic ignimbrite (slightly kaolinized), 3) Dacito-andesitic ignimbrite (intensively kaolinized), 4) Dacito-andesitic ignimbrite (unaltered), 5) Siderite, 6) Dacito-andesitic ignimbrite, with galena impregnations
Slika 2. Detajl rudne žile št. 10, rudišče Zletovo
1) Pb-Zn ruda, 2) slabo kaoliniziran dacitsko-andezitski ignimbrit, 3) močno kaoliniziran dacitsko-andezitski ignimbrit, 4) nespremenjen dacitsko-andezitski ignimbrit, 5) siderit, 6) dacitsko-andezitski ignimbrit z impregnacijami galenita

as with pyrrhotite, marcasite and magnetite, which were found only sporadically. Minor occurrences of U-mineralisation represented by pitchblende have also been observed.

The morphological and geological characteristics of the ore veins from the Zletovo Mine are in general represented by the main characteristics of the ore vein No. 10 which was studied in detail (Fig. 2). From Figure 2 it is clearly evident that the central parts of the vein are composed of massive ore while the outer parts are hydrothermally altered and only slightly impregnated by ore minerals. Hydrothermal alterations are mostly silicification and kaolinitization. The concentration of ore minerals in the central part is more than 20 % Pb+Zn, while the altered mineralised vein zones exhibit a considerably lower Pb+Zn content of about 3 %.

MATERIALS AND METHODS

For the purpose of this study the hydrothermal ore veins in the Zletovo Mine were sampled at different levels. The sampling was possible because the exploitation of the mine was in progress. During the field work representative samples for ore microscopy and for further electron microprobe analysis of sulphides and sulphosalts were taken. All the samples were macroscopically selected for the polished sections. Polished sections of the ore samples were first examined under a ZEISS Axiolab Polarizing Microscope equipped with a photographic camera. After this the selected samples of ore minerals and sulphosalts were analyzed for their S, Fe, Co, Cu, Zn, Ge, As, Ag, Cd, In, Sn, Hg, Pb and Bi contents by WDS electron microprobe using a CAMECA/CAMEBAX equipment.

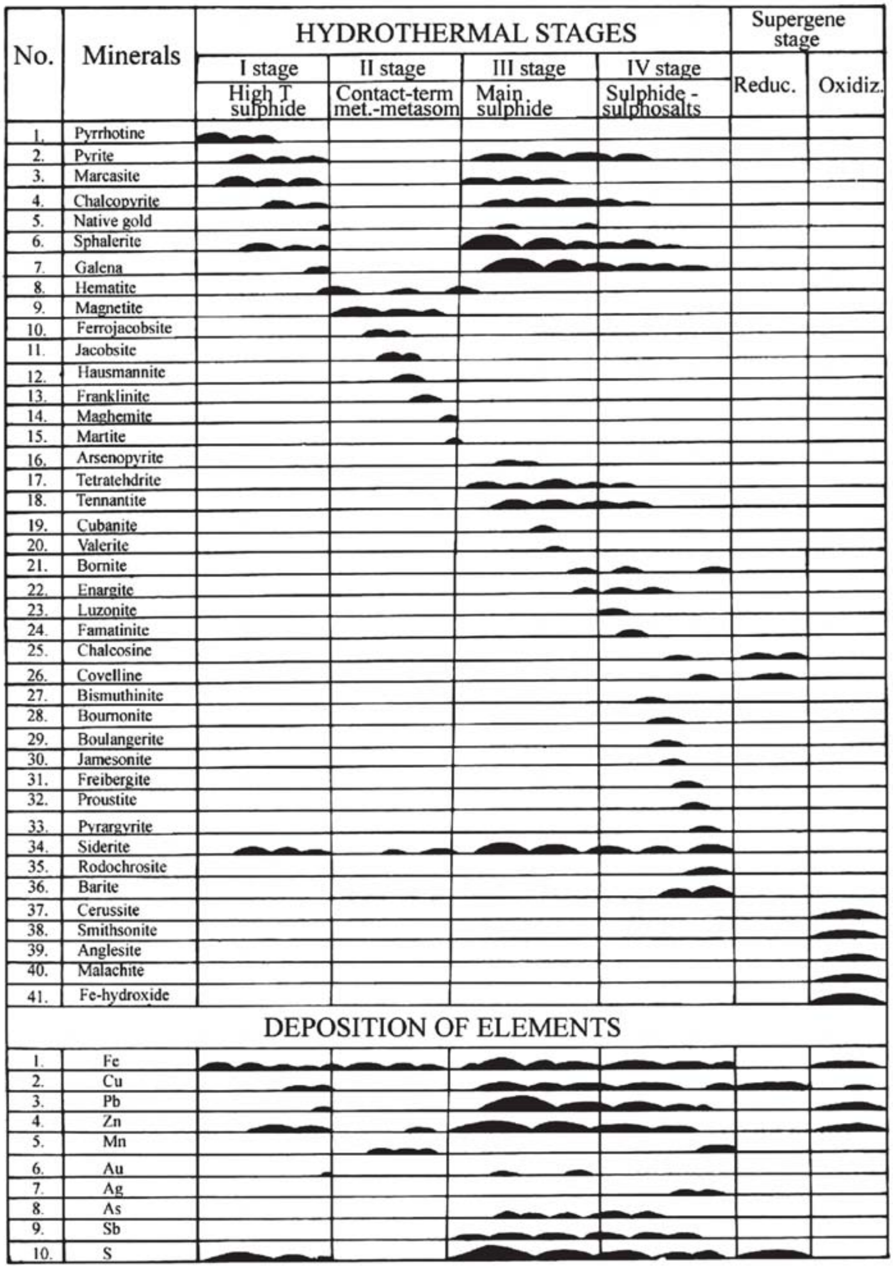


Figure 3. Paragenetic sequences in the Zletovo ore deposit (Serafimovski, 1990)
Slika 3. Paragenetsko zaporedje mineralov v rudišču Zletovo (Serafimovski, 1990)

The analytical precision for Sb, Zn, As, and Ag was 1–3 %, 3–10 %, 10–15 % and 10-15 %; however, it was somewhat lower for Pb, Cd, In and Sn, i.e. 2–5 %, 5–15 %, 15–30 % and 15-25 %, respectively. Detectable concentrations of Sn and In were only found in some tetrahedrites, while the Co, Ge, Hg and Bi contents in the tetrahedrites were always below the detection limits of the instrument. The detection limits for Hg and Bi were very high, and usually between 0.4 and 0.6 %. This is most probably due to the interference between the different element´s X-ray spectra. As and Pb were also characterized by high detection limits, usually of 0.25 %, relative to those for the other elements such as Fe (0.05 %), Co and Cu (0.07 %) as well as for Zn, Ag, In, Sn, Cd and Ge with detection limits between 0.1 and 0.13 %.

RESULTS AND DISCUSSION

The results of previous investigations together with the results of the presented study confirm the complex mineral composition of the Pb-Zn mineralization in the Zletovo ore deposit. More than 40 ore bearing and gangue minerals were identified. All of them were crystallized successively from the ore bearing hydrothermal solutions during a few ore bearing stages, thus building complex paragenetic relations. An overview of ore minerals and their sequence of deposition in the frame of the ore forming stages are given in Figure 3. The micro-morphological characteristics and the appearance of the main ore minerals, their relations and the relations of some other minerals are presented in Figure 4.

Major ore bearing minerals

Galena and sphalerite are the main and the most important ore minerals in the Zletovo Pb-Zn ore deposit, followed by pyrite, chalcopyrite, tetrahedrite, tennantite, marcasite, siderite and partially barite, pyrrhotite, enargite, bornite, arsenopyrite and chalcocite. Magnetite, jacobsite, hematite, hausmannite and others occur only sporadically. All other ore minerals not mentioned here were mostly found in trace amounts and have no economic importance. It should be pointed out that in some ore veins the quantitative ratios of the main ore minerals are changeable. For example, in ore vein No. 1 galena and sphalerite prevail, while the next most common mineral is siderite. On the other hand in ore vein No. 10 pyrite is the main ore mineral, followed by other sulphides. However, in general, galena and sphalerite are the most common and the most important ore minerals even if they were deposited in different morpho-logical types of mineralization.

Sphalerite was only found in few generations, and in some of them it shows exsolved structures of chalcopyrite due to the decomposition of solid solution sphalerite-chalcopyrite. Most often it is metacolloidal to collomorph with zonal patterns and internal reflections. The crystal forms are very rare. More often it is found in over-growth with galena, chalcopyrite and tennantite. Sometimes it metasomatically replaces galena, although in some places it looks like to be suppressed by them. Here and there sphalerite is cataclastic and interstitionally replaced by quartz, galena, tennantite and other minerals. Sphalerite is also myrmekitically interlocked with galena, chalcopyrite, tetrahedrite and other ore minerals.

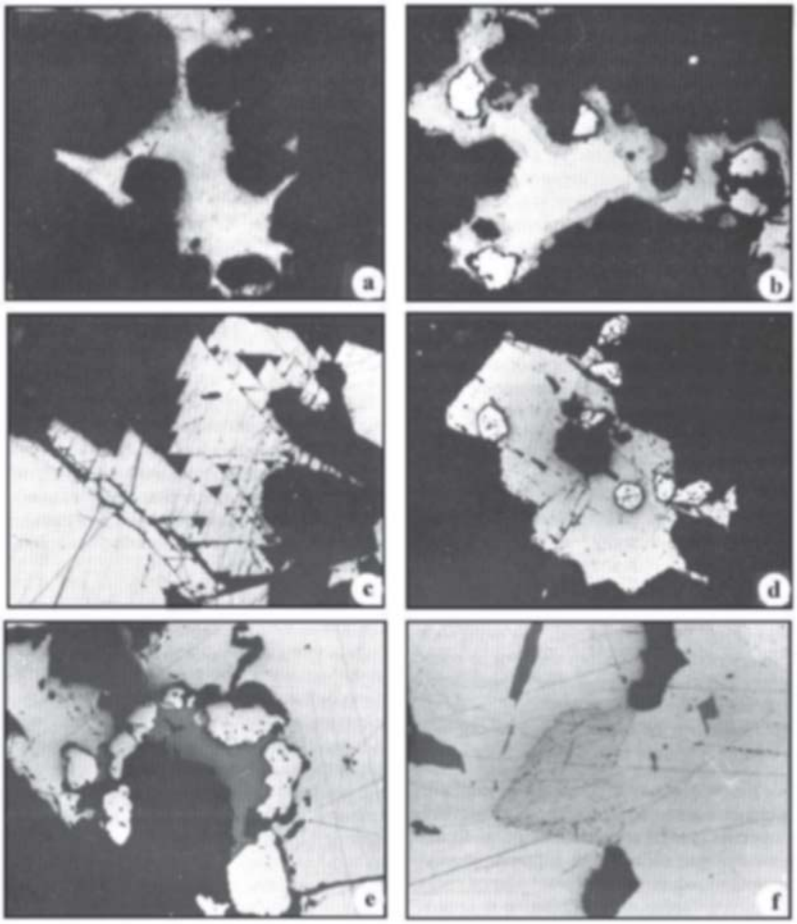


Figure 4. Micro-morphologic shapes and the occurrence modes of galena in the Zletovo ore deposit (Serafimovski, 1990): **a)** Metasomatic replacement of galena (white) by well developed quartz crystals (dark). Reflected polarized light, 100x; **b)** Corosion of chalcopyrite (white) by galena (grey-white) along intestices and the replacement of galena (white grey) by quartz (dark). In the galena there are remains of pyrite (light), while along its borders there is tennantite (grey). Reflected polarized light, 100x; **c)** Cataclized galena crystal (white) suppressed by quartz (dark). Reflected polarized light, 100x; **d)** Pyrite remains (white) in galena (white grey) with the presence of quartz (dark) of metasomatic origin. Reflected polarized light, 100x; **e)** Corrosion of galena (white grey) by tennantite (dark grey) and tennantite by quartz (dark). At the contact between the galena and tennantite are the remains of ring forms of pyrite. Reflected polarized light, 100x; **f)** Hypidiomorphic grain of bournonite (dark grey) in massive galena (grey). Reflected polarized light, 100x.

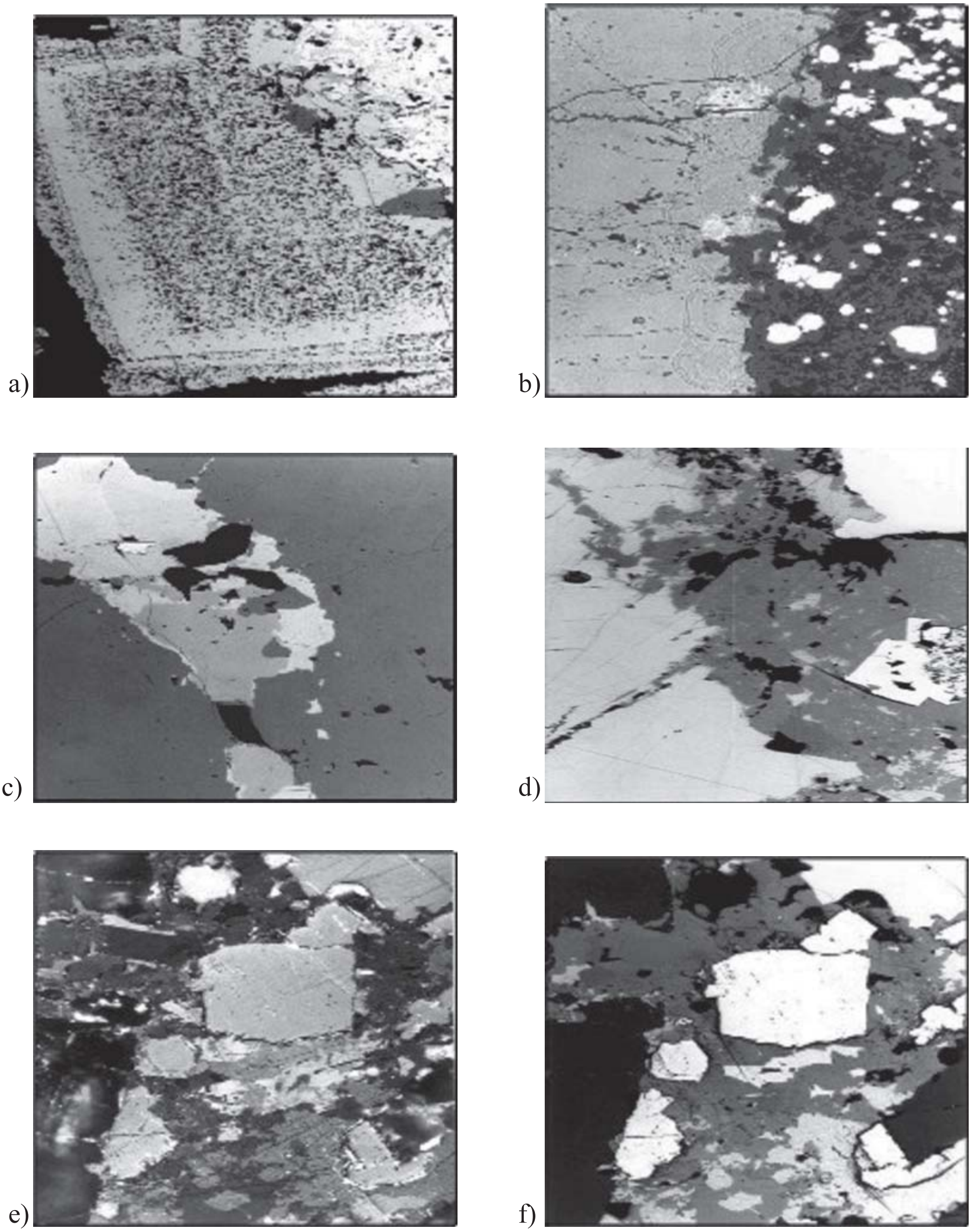
Slika 4. Mikromorfološke značilnosti galenita iz rudišča Zletovo (Serafimovski, 1990): **a)** metasomatsko nadomeščanje galenita (belo) s kremenom (temno), odsevna polarizirana svetloba, 100x, **b)** nadomeščanje halkopirita (belo) z galenitom (svetlosivo) in galenita (svetlosivo) s kremenom (temno), odsevna polarizirana svetloba, 100x, **c)** kataklazirana galenitova zrna (belo) cementira in nadomešča kremen (temno), odsevna polarizirana svetloba, 100x, **d)** ostanki pirita (belo) in galenita (svetlosivo) ter metasomatski kremen (temno), odsevna polarizirana svetloba, 100x, **e)** nadomeščanje galenita (svetlosivo) s tennantiton (temnosivo) in tennantita s kremenom (temno). Na stiku med galenitom in tennantitom so ostanki pirita obročaste oblike, odsevna polarizirana svetloba, 100x, **f)** hipidiomorfno zrno bournonita (temnosivo) in masivni galenit (sivo), odsevna polarizirana svetloba, 100x.

Table 1. Results of electron microprobe analyses of sphalerite (1-10), pyrite (11, 12), arsenopyrite (13) and galena (14, 15) from the Zletovo ore deposit (in %)
Tabela 1. Rezultati geokemične analize rudnih mineralov iz rudišča Zletovo z elektronskim mikroanalizatorjem: (1-10) sfalerit, (11,12) pirit, (13) arzenopirit, (14, 15) galenit). Elementna sestava je v %.

Elements	S	Mn	Fe	Cu	Zn	Ga	As	Cd	Sb	Pb	
1	30,5	0,0	0,3	0,0	68,7	0,0	0,0	0,5	0,0	-	100,0
2	31,0	0,0	0,4	0,0	67,8	0,3	0,0	0,5	0,0	-	100,0
3	30,3	0,0	0,6	0,0	68,0	0,0	0,0	0,0	0,1	-	100,0
4	30,4	0,0	6,5	0,0	69,1	0,0	0,0	0,0	0,0	-	100,0
5	34,2	0,1	0,4	0,0	65,3	0,0	0,0	0,0	0,0	-	100,0
6	38,5	0,2	0,8	0,0	58,8	0,0	0,8	0,4	0,0	-	100,1
7	40,4	0,0	0,6	0,0	59,6	0,0	0,0	0,0	0,0	-	100,1
8	30,7	0,0	0,5	0,0	58,5	0,0	0,0	0,3	0,1	-	100,1
9	35,0	0,0	0,0	0,0	64,7	0,0	0,0	0,3	0,0	-	100,0
10	30,7	0,0	2,8	3,7	62,7	0,0	0,0	0,0	0,1	-	100,1
11	51,8	0,0	47,5	0,2	0,4	0,0	0,0	0,2	0,0	-	100,1
12	49,2	0,0	50,2	0,0	0,0	0,0	0,7	0,0	0,0	-	100,1
13	23,1	0,0	37,1	0,2	4,1	0,0	35,0	0,0	0,6	-	100,1
14	20,5	-	-	-	1,0	-	-	-	-	78,6	100,1
15	20,5	-	-	-	1,1	-	-	-	-	78,6	100,1

Figure 5. (next page) Microphotographs of sulphides and sulphosalts from the Zletovo ore deposit (ore vein No.10) analyzed by electron microprobe: **a)** Late generation of zoned galena crystal rich in quartz inclusions. Earlier generation of galena-sphalerite-pyrite-tetrahedrite ore minerals are the background where the galena crystal was growing. Reflected polarized light, 67x; **b)** Contact between intensively pyritized volcanic rock fragment and massive sphalerite (gray). Reaction with hypochloric NaOH at the borderline confirmed the presence of zinc sulphide with zoned composition. Reflected polarized light, 67x; **c)** Sphalerite cutting by the vein containing galena (light gray), tetrahedrite (gray), chalcopyrite (medium gray, upper part), quartz and traces of pyrite. Reflected polarized light, 270 x; **d)** Ore composed of pyrite (white), chalcopyrite (light gray, left part), tennantite (gray in lower and central part) with inclusions of galena (light gray) and luzonite-stibioluzonite (dark gray, lower central part). Reflected polarized light, oil immersion, 430 x; **e)** Complex mixture of pyrite (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). Reflected polarized light, oil immersion, 430x; **f)** Partially crossed nicols. Note the lamellar twinning in one direction of the luzonite-stibioluzonite (light to middle gray, central and lower part), and the "flashy" internal reflections of tennantite (dark gray, left part).
Slika 5. (naslednja stran) Slike sulfidov in sulfosoli iz rudne žile št. 10, analiziranih z elektronskim mikroanalizatorjem, rudišče Zletovo: **a)** Mlajša generacija conarnega galenita z vključki kremena. Osnovo v kateri je kristal rastel predstavlja starejša mineralna parageneza galenit-sfalerit-pirit, odsevna polarizirana svetloba, 67x, **b)** stik med odlomkom močno piritizirane vulkanske kamnine in masivnim sfaleritom (sivo). strukturno jedkanje je odkrilo na stiku conarno zgradbo sfalerita, odsevna polarizirana svetloba, 67x, **c)** sfaleritno polje seka žilica, ki vsebuje galenit (svetlosivo), tetraedrit (sivo), halkopirit (srednje sivo), kremen (temno) in sledove pirita, odsevna polarizirana svetloba, 270x, **d)** polimineralno polje sestavljeno iz pirita (belo), halkopirita (svetlo sivo), levi del slike), tennantita (sivo, spodnji in osrednji del slike) z vključki galenita (svetlo sivo) in luzonitom-stibioluzonitom (temno sivo, spodji osrednji del slike), odsevna polarizirana svetloba, oljna imerzija, 430x, **e)** polimineralna ruda sestavljena iz pirita (belo), sfalerita (temno sivo) galenita (belo), halkopirita (svetlo sivo, osrednji del slike) tennantita (srednje do temno sivo) in luzonita-stibioluzonita (temno sivo, močno pleohroično, srednji del slike), odsevna polarizirana svetloba, oljna imerzija, 270x, **f)** ista slika, ne povsem + nikoli. Opazne so dvojčične lamele luzonita-stibioluzonita potekajoče v eni smeri (srednji in spodji del slike) in notranji refleksi v tennantitu (temno sivo, levi rob slike), odsevna polarizirana svetloba, oljna imerzija, 270x.

The composition of the sphalerite in the Zletovo deposit is close to the normal values of the theoretically determined values for sphalerite (Criddle and Stanley, 1986). The exception is the Fe content, which in some sphalerites is up to 6.5 % (Table 1). In addition to Fe, sphalerites also contain small quantities of Mn and Cd.



Galena was also found in a few generations. In contrast to sphalerite it shows a high degree of crystallinity and very often well-developed crystals. The most beautiful crystal forms of galena can be found in the open veins and vugs as well as in the fracture zones. Here and there the galena crystals are cataclastized and exhibit well developed cleavages and extensive replacement with quartz (Fig. 4). The extend of galena replacement by quartz is sometimes so large that only some remains are left of the primary galena grains. In some places the galena develops along the interstices with pyrite and encloses the pyrite remains, while at other locations it is intensively overgrown with bournonite and other sulphosalts.

Galena is usually suppressed by sphalerite, chalcopyrite, tetrahedrite and tennantite, but with these minerals it is also myrmekitically interlocked and forms emulsions. Sometimes dispersive entrapment of pyrite, arsenopyrite and other sulphides can be observed. The elemental composition of galena in the Zletovo Mine is very close to the theoretical values. Microprobe analyses also showed the presence of Zn and Ag in the galena structure (Table 1).

Sulphosalts and ore bearing minerals from vein No. 10

The already known mineral assemblage composed mainly of galena, sphalerite, pyrite, chalcopyrite, siderite and other ore and gangue minerals is supplemented with sulphosalts. During this study special attention was given to ore vein No. 10. From this ore vein five representative samples for ore microscopy and further electron microprobe analyses were taken. Microscopic and electron microprobe analyses revealed tetrahedrite-tennantite solid solution compositions as well as sulphosalt minerals such as luzonite, stibioluzonite and pearceite (Fig. 5). The composition of particular minerals and the phases of interest found during this study are presented in Table 2 and 3. Their main characteristics are given below:

Luzonite Cu_3AsS_4

Luzonite was found in samples Z-3 and Z-5. The luzonite from samples Z-3 is slightly more Fe rich (0.15–0.66 %) and contains less Sb (0.17–2.5 %) relative to the luzonite from samples Z-5, which has only up to 0.14 % Fe and 1.7–3.8 % Sb. The luzonite from samples Z-3 also contains a minor amount of Zn (≤0.26 %), Ag (≤0.17 %) and Cd (≤0.15 %). These elements in the luzonite from samples Z-5 are absent or found in lower concentrations. The elemental composition close to the standard values for luzonite was obtained for the luzonite from sample Z-5-3 Lu2 (Table 2).

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

Pearceite with 59 % Ag and a ratio $Sb/(Sb+As)_{mol}$ = 0.14 was found in sample Z-5 as rare, small grains associated with Luz+Ten+Gal+Py+Cp. The closest composition to the standard values for this mineral was obtained for the pearceite from sample Z-5-2 Pea3 (Table 2).

Tetrahedrite $Cu_{12}Sb_4S_{13}$ – Tennantite $Cu_{12}As_4S_{13}$

The tetrahedrites from Zletovo are members of the tetrahedrite-tennantite solid solution [$Sb/(Sb+As)_{mol}$ = 0.04 - 0.94]. They are

Table 2. Results of electron microprobe analyses of pearceite (Pea) and luzonite (Lu); ore vein No. 10, Zletovo ore deposit (in %)

Tabela 2. Rezultati geokemične analize pearceita (Pea) in luzonita (Lu) z elektronskim mikroanalizatorjem. Rudišče Zletovo, rudna žila št. 10. Elementna sestava je v %.

Element	Z-5-2Pea3	Z-5-2Lu3	Z-5-2Lu4	Z-5-3Lu2	Z-3-5Lu	Z-3-5Lu	Z-3-1Lu6	Z-3-1Lu7
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

enriched in Zn, usually 7 - 8 %, and Ag the concentration of which is up to 5.5 % (Table 3). The Fe content is always relatively low, and usually below 1 %. Within the individual samples, elevated concentrations of Ag were found in the more Sb-rich grains or in clusters of grains, and this decreases in the more tennantitic-rich solid solutions. The highest Ag contents are found in small, few micrometers thick droplet-like inclusions of tetrahedrite inside the galena crystals from Gal+Sph+Pyr±Tet/Ten veinlets. These inclusions seem to represent the main Ag reservoir of the previously reported Ag-bearing Zletovo galenas with up to 1250 ppm Ag (Mudrinić and Petković, 1982). The Cd content in the investigated droplets is usually below 0.3 %, although some of them exhibit considerably higher concentrations of up to 1.1 %. One of the droplets also had a detectable in content of about 0.15 %. The Sn concentrations are just above the detection limit (0.10–0.12 %) and were found only in the more Sb-rich compositions. In samples with a coarser texture the tetrahedrite–tennantite composition is characterized by an intermediate $Sb/(Sb+As)_{mol}$ ratio of 0.44. The contamination due to an overlap with neighbouring phases may have affected the analysis of the fine grained tetrahedrites, reflected in locally very high Pb contents (up to 0.4 %). The closest composition to the standard values is shown in an analysis of tethraedrite from the sample Z-3-5Tet2 (Table 3).

Tennantites, as the other end-member of the tetrahedrite-tennantite solid solution series, exhibit elevated concentrations of Zn (1.72–8.33 %) and Sb (1.32-7.38 %) and a relatively low Fe content (0.1-3.06 %). Within different tennantite grains, the amount Ag decreases toward the more tennantitic compositions. The Cd content can also be

Table 3. Results of electron microprobe analyses of tennantite (Ten) and tetrahedrite (Tet), ore vein No. 10, Zletovo ore deposit (in %)
Tabela 3. Rezultati geokemične analize tennantita (Ten) in tetraedrita (Tet), z elektronskim mikroanalizatorjem. Rudišče Zletovo, rudna žila št. 10. Elementna sestava je v %.

Element	Z-3-4 Ten	Z-3-1 Ten 4	Z-5-2 Ten 2	Z-5-2 Ten 3	Z-3-5 Tet 1	Z-3-5 Tet 2	Z-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

significant, with concentrations between 0.17 and 0.61 %. In was only detected in concentrations of 0.01 and 0.07 %. The Sn content is only slightly above the detection limit (0.01-0.05 %). The closest composition to the standard values was found for an analysis of sample Z-5-2 Ten2 (Table 3).

Galena

Galena is almost pure PbS. Elevated concentrations of Cu (≤0.7 %), Zn (<0.4 %), Fe (0.16 %) and possibly Cd (≤0.16 %) were found only in some samples. These elements could be related to fine inclusions of unresolved sulphides.

Sphalerite

Sphalerite is characterized by low Fe contents (usually ≤1 %). Higher Fe concentrations were measured only in samples Z-3 (≤6 %) and Z-5 (≤2 %). Grain-to-grain and within-grain variations in Fe concentrations show no clear textural dependence. The highest Fe contents are typically associated with the lowest Cd concentrations which are in sphalerite, with a minimum Fe content between 0.5 - 0.8 %. Minor amounts of Cu, Sb and Pb were also detected in some sphalerites. The late generations of sphalerite, for example, schalenblende in sample #3, are distinctly cathodoluminescent and represent almost pure sphalerite with only a detectable As content (0.3 %) and low Cd concentrations (0.15 %).

Calchopyrite

Chalkopyrite is very pure $CuFeS_2$ with trace elements content below the detection limits of the equipment.

Pyrite

All the analyzed generations of pyrite are considerably enriched in As. This enrichment could be related to very fine unresolved intergrowth textures with arsenopyrite, as suggested by the crystal chemical formulae (S+As=Fe). Minor contents of Cu (≤0.7 %) were only measured in late generations of euhedral and/or partially corroded pyrite grains from Gal±Sph±Tet±Ten±Luz+Pyr mineral assemblages. Pyrite grains related to an early pyritization stage are virtually Cu free. An exception are samples Z-5 in which pyrite revealed an elevated Cu content of about 0.36 % and high As concentrations around 4.4 %. Detectable Pb (≤0.26 %) and Zn concentrations (≤0.4 %) were occasionally found both in early and in late generations of pyrite as well as in partially resorbed pyrite grains. More information about the mineral parageneses and geochemical features of the major minerals in ore veins can be found in Mudrinić and Serafimovski (1990; 1991) and Serafimovski and Tasev (2003).

Conclusions

The results from the latest field and laboratory studies of samples from different ore veins confirmed the mineral paragenesis characteristic for hydrothermal conditions of origin and revealed the very complex polymetallic characteristics of the Zletovo Pb-Zn mine. A detailed study of ore vein No. 10 and its border parts indicated that the main ore minerals are represented by the prevailing galena and sphalerite followed by tetrahedrite, tennantite, pyrite, chalcopyrite, quartz, calcite, siderite as well as other less important ore and gangue minerals. The electron microprobe analyses of the galena and sphalerite showed that their compositions mostly exhibit the theoretical values for those minerals (with minor impurities related to some characteristic trace elements). A detailed study by electron microprobe further revealed that the tetrahedrite and tennantite form solid solution phases with compositions ranging from pure tetrahedrites, through mixed solid phases to pure tennantites. This phenomenon was for the first time found in the Zletovo mine during this study and deserves further investigation. A detailed study of the sulphosalts confirmed the presence of luzonites and pearceites, while some separate phases looked like seligmannite. Our intention to determine silver sulphosalts was not successful; however we will make this the subject of future studies.

Acknowledgement

For all his efforts during the field sampling of the Zletovo Mine and for help with the laboratory analysis of the samples we express our sincere gratitude to our colleague dr. Paolo Nimitz from the Department of Mineralogy and Petrology, University of Padova, Italy. Thanks also to Dr. Paul McGuiness for linguistic corrections.

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