# PECULIARITIES OF Pb-Zn MINERALISATION IN DEPOSITS FROM YUGOVO ORE FIELD

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#### ABSTRACT

Samples from quartz-galena-sphalerite mineralisation in Yugovo ore field have been studied (from ore occurrence Braikovitza and Komin dere). The mineralisation is related to small Early Alpine granitoid bodies, probably of Late Cretaceous age, intruded in metamorphic rocks from Dobrostan formation. The mineral composition of the ore is described and data on trace elements content in galena (atomic absorption analyses) are presented. Isomorphic presence of Ag and Bi in galena is proved through microprobe investigations. The composition of aikinite inclusions in galena is also studied. The temperature interval of mineral crystallisation (homogenisation of fluid inclusions in quartz from productive mineral paragenetic association) is in the range of 360 – 300° C. Key words: – Pb-Zn mineralisation, fluid inclusions, trace-elements.

### INTRODUCTION

The Yugovo ore field is situated in the northern part of the Central Rhodope ore district (Dimitrov, 1988) and according to some authors – within the confines of the so-called Yugovo-Narechen ore district (Maneva et al., 1989). The ore field is located from Yugovo road fork on the North to the town of Laki to the South and comprises molybdenite, lead-zinc and fluorite mineralisatons. The Mo mineralisation is of quartz-molybdenite type (ore occurrences Yugovsko hanche, St. Georgi, Laki), the Pb-Zn one is of quartz-galena-sphalerite type (ore occurrences Braikovitza and Komin dere) and the F mineralisation is of quartz-fluorite-sulphide type (deposit Yugovo, ore occurrences Gugliovo, Propula, Borovo).

The ore mineralisation is related to a small granitoid intrusive bodies of Late Cretaceous age – leucocratic granite and granodiorite (the so-called Yugovo granitoids – Stoynova et al., 1984; Nedyalkov et al., 1998).

Quartz-molybdenite veins are not of economic interest. Quartz-galena-sphalerite mineralisation is mainly of vein type – steep dipping veins with sub-equatorial and northeastern direction, cross-cutting schists and marbles of Dobrostan and Yavrovo formations (Fig. 1). Metasomatic replacement ore bodies are also present (in skarns of ore occurrence Komin dere). Ore veins could be traced on the surface to 700 m, with thickness usually not exceeding 1 m. Fluorite veins are mainly of sub-equatorial orientation and represent infillings of quartz, sometimes quartz plus carbonate with dissemination, nests and rarely lenses of barite-fluorite-celestine and sulphide mineralisation. Metasomatic lens-like fluorite bodies in marble layers also occur. The lead-zinc mineralisation could be assumed as a subfacies of fluorite-barite-sulphide mineralisation, well manifested in Yugovo deposit.



Figure 1. Schematic geological map of Yugovo ore field (after Stoynova et al. 1984, Ivanov et al. 2000).
Abbreviations on inset map: MP – Moesian Plate; B – Balkanides; SG – Srednogorie Zone; R – Rhodopes; Y – Yugovo ore field.

 Oligocene trachyrhyolite and rhyodacite (a- subvolcanic bodies, b- dykes); 2. latite; 3. Eocene-Oligocene volcanosedimentary unit; 4. Upper Cretaceous granitodes; 5. parametamorphites from Dobrostan and Yavrovo formations;
 orthometamorphites from Bachkovo formation; 7. faults; 8. ore deposits and ore occurrences: 1- Yugovo, 2- Braikovitza,
 Komin dere, 4- Laki, 5- Propula, 6- Borovo, 7- St. Georgi, 8-Yugovsko hanche In quartz-molybdenite veins, main ore minerals are pyrite and molybdenite, arsenopyrite and pyrrhotite are abundant (Stoynova, 1988; etc.). The mineral composition of the quartzfluorite-barite veins is quartz, fluorite, barite, calcite, manganocalcite (Todorov, 1989); rare minerals are bastnesite, gypsum plus small amount of sulphides – almost all of the established in the Pb-Zn mineralisation.

### Pb-Zn MINERALISATION

Three mineral paragenetic associations (mpa) in the quartzgalena-sphalerite mineralisation can be distinguished: quartzpyrite, quartz-sphalerite-galena (productive) and carbonate one. In the productive mpa besides quartz, galena and sphalerite, also fluorite, molybdenite, chalcopyrite, tetrahedrite, tennantite and aikinite are established and as rare ones bismuthinite, cosalite, galenobismuthite and tetradymite (Stoynova, 1988).

Typical for the ores is higher content of F, Ba and Mo and also presence of Sr. In the composition of quartz-galenasphalerite mineralisation, lead strongly prevails (geochemical type Pb>>Zn). Galena usually is fine- to medium-grained, most often as nests and dissemination in quartz, rarely forming massive aggregates with coarse-grained texture.

Main trace elements in galena are Ag and Bi – establishedin all analysed samples (Table 1). The content of Ag is in the range from 661 to 5610 ppm (average 4015 ppm), while Bi is from 942 ppm to 25400 ppm (average 15783 ppm).

Table	e 1.	Trace	e elements	in i	galena	from	ore o	occurr	rence	Braik	ovitza	(atomio	c abso	rption	analy	yses	of n	nonor	ninera	sam	ples	).
												1 1	1 .									

No		Sampla No						Elemer	it conter	nt (ppr	า]				
		Sample No	Ag	Sb	Bi	Te	Se	Cd	TI	Sn	Zn	Fe	Cu	Mn	Со
I	1	1	1501	-	4155	41	42	49	-	20	1286	100	347	-	29
	2	2	661	50	942	168		56	2	2	238	10	225	5	23
	3	23 I	5610	30	24900			160	70	20	14700	900	3730	110	60
	4	26 II	5570	-	17400	157	62	180	1	1	21200	1200	2630	140	60
	5	34 II	5350	50	25400	130	3	130	100	7	310	160	3340	30	60
	6	35 II	5400	10	22400	93	19	180	100	7	180	500	2430	15	60
			1 12 1 1	• •			10	6					0	-	

The content of Cu is relatively high and correlates well with the content of Bi. It is in the range from 225 to 3730 ppm (average 2117 ppm).

Among the other trace elements, a relatively constant and high content of Te and Cd should be mentioned (no correlation between Cd content and presence of Zn is observed), as well as presence of Tl and Se.

Microprobe analyses of homogenous galena grains were provided (Table 2). The homogeneity of analysed galena grains was investigated – not only under optical microscope, but also in scanning electron microscope (Plate A). For the same area, data for regular distribution of Ag were obtained (Plate B), as well as for Bi, but with lower density. Ag and Bi were proved in all samples with average content 0.55% and 0.18% respectively while Te was found in two cases. Sb and Cd in analysed samples are in quantities under the threshold of response of the method. The contents of Ag correspond to those established by atomic absorption analysis, while the content of Bi is significantly lower. This could be explained by presence of numerous small aikinite inclusions in galena, the larger of them being observed in reflected light microscope.

Table 2. Microprobe analyses* of ga	alena
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No	Sample	Element content [wt. %]										
	No	Ag	Bi	Te	Pb	S	Σ					
1	23	0.62	0.54	-	85.33	13.87	100.36					
2	23 I	0.40	0.09	-	85.08	13.70	99.27					
3	23	0.47	0.18	-	84.14	13.63	98.42					
4	35 II	0.57	0.02	-	83.79	13.74	98.12					
5	35 II	0.51	0.13	0.04	84.51	13.33	98.52					
6	35 II	1.30	0.13	0.06	83.75	13.24	98.48					

\* Sb and Cd not found

Balance of atomic quantities of Ag, Cu, Sb and Bi in galena shows atomic ratios Ag:(Sb+Bi) and Cu:(Sb+Bi) close to 1:2 (Table 3). Due to the low content of Sb, these are practically atomic ratios Ag:Bi and Cu:Bi. Atomic ratios (Ag+Cu):(Sb+Bi) are close to ratio 1:1, which correspond to bonding of Ag and Cu with Bi as matildite and aikinite (Fig. 2). The presence of Ag and Cu could be explained with limited solid solution matilditegalena, formed at temperature over 216° C (Vaughan and Craig, 1978) and inclusions of aikinite (probably even of submicronic size).

Table 3. Atomic quantities of Ag, Cu, Sb and Bi in galena from ore occurrence Braikovitza and atomic ratios (according to the analyses in Table 1)

No	A	tomic x 10	quantii 0 000	ties	Ag:(Sb+Bi)	(Ag+Cu):(Sb+Bi)
	Ag	Cu	Sb	Bi		
1	139	55	-	385	1:2.77	1 : 1.98
2	61	35	4	87	1 : 1.5	1 : 0.95
3	520	587	2	1192	1 : 2.29	1 : 1.08
4	516	414	-	833	1:1.61	1:0.9
5	496	526	4	1215	1 : 2.46	1 : 1.19
6	501	382	1	1072	1:2.14	1 : 1.22

Presence of aikinite in ore from Braikovitza was reported by Gadjeva in 1972. Later Stoynova and Begizov (1982), using microprobe analyses and powder diffraction method, proved aikinite in mineralisations from ore occurrence Komin dere.

Investigation of polished sections from ore occurrences Braikovitza and Komin dere through reflected light microscope and microprobe analyses show presence of aikinite in the ore – most often at the periphery of galena grains (Plate C) or as cross-cutting veinlets (Plate D). Small aikinite inclusions with irregular shape in galena were also observed in some cases,





Fig. 2. Atomic ratios (Ag+Cu):(Sb+Sb) – according to Table 3

ChTable 4). Other analyses show the composition of larger grains or veinlets of aikinite in galena (analyses 9, 10, Table 4).aracteristic for the aikinite studied is almost absolute absence of impurities and constant crystallo-chemical formula, close to the theoretical one, with an exception of the last two analyses, made on aikinite veinlets that cross-cut galena.

Fluid inclusion studies were provided using method of homogenisation of vapour-liquid inclusions in quartz from productive quartz-sphalerite-galena mpa. Fluid inclusions are relatively small in size (up to 20-30, rarely 50  $\mu$ m) with ratio vapour : liquid from 1 : 8 to 1 : 3, rarely higher. All fluid inclusions studied homogenise in vapour phase in temperature interval from 250 to 370° C. Column chart showing distribution of temperatures of homogenisation of fluid inclusions for ore occurrences Komin dere and Braikovitza are given on figures 3 and 4.

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			El	ement co	ntent [w	Formula			
No	Pb	Cu	Fe	Bi	Sb	Te	S	Σ	Fornula
1	36.64	11.90	-	34.00	-	-	17.12	99.66	Pb1.00Cu1.06Bi0.92S3.02
2	35.46	11.12	-	36.71	-		16.17	99.46	Pb1.00Cu1.02Bi1.03S2.95
3	34.82	11.86	-	36.96	-	-	16.41	100.05	Pb0.97Cu1.07Bi1.02S2.94
4	33.04	11.84	-	37.17	-	-	17.29	99.34	Pb <sub>0.90</sub> Cu <sub>1.05</sub> Bi <sub>1.00</sub> S <sub>3.04</sub>
5	34.14	11.37	-	38.01	-	-	16.71	100.23	Pb <sub>0.94</sub> Cu <sub>1.03</sub> Bi <sub>1.04</sub> S <sub>2.99</sub>
6	34.71	11.94	-	36.01	0.50	-	16.15	99.31	Pb0.97Cu1.09(Bi1.00Sb0.02)1.02S2.92
7	36.69	11.48	-	35.55	-	-	16.65	100.37	Pb1.01Cu1.04Bi0.97S2.98
8	33.83	11.05	-	38.20	0.39	-	16.68	100.15	Pb0.94Cu1.00(Bi1.05Sb0.02)1.07S2.99
9	35.56	11.39	0.22	35.31	0.56	0.43	16.42	99.89	Pb0.99(Cu1.03Fe0.02)1.05(Bi0.97Sb0.03)1.00(S2.94Te0.02)2.96
10	34.16	10.99	0.14	37.31	-	0.25	17.32	100.17	Pb0.93(Cu0.98Fe0.01)0.99Bi1.01(S3.05Te0.01)3.06

In ore occurrence Komin dere, a well expressed maximum is observed within the temperature interval 350–310° C. In ore occurrence Braikovitza, two maximums of homogenisation temperatures are present: 290–270° C and 350–310° C. The maximum at lower temperature is most probably connected with secondary inclusions. According to Krasteva and Todorov (1986), deposition of quartz-fluorite-barite mineralisation took place from 270° to 100° C, while deposition of late quartz and carbonate was within the temperature interval 150–50° C.

## CONCLUSIONS

The Pb-Zn mineralisation in ore occurrences Braikovitza and Komin dere is quite different from the mineralisation in Tertiary Pb-Zn deposits from Laki ore field both mineralogically and geochemically.

The mineralisation in Yugovo ore field is genetically related to granitoid intrusive bodies and a magma chamber in depth – processes, which took place before the formation of the Tertiary Central Rhodope Dome (Ivanov et al., 2000).

Model ages, based on isotope composition of lead in galena, are in average as follows: uranogenic -76 Ma, thorogenic -68 Ma (Amov et al., 1993).

A genetic connection of the Pb-Zn mineralisation with Upper Cretaceous igneous rocks is proved by similarity in lead isotope composition both in granitoids and galena from ores.

Ratios <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb for granitoid rocks from Laki and Yugovo plutons are as follows: 18.624, 15.669, 38.800 and 18.641, 15.651, 38.738, respectively. The





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Plates:

Plate A. Homogenous galena. Backscattered electron image, COMPO regime. Plate B. The same observation field as on Plate A. Distribution of Ag in characteristic rays. Plate C. Galena-aikinite aggregate among gangue minerals (black). Aikinite is grey in colour, galena – white. Backscattered electron image, COMPO regime. Plate D. Aikinite veinlet (1), cross-cut galena (with different shade from light grey to white due to uneven carbon coating. Backscattered electron image, COMPO regime.



T hom [deg. C]

### Figure 4. Histogram showing temperatures of homogenisation of fluid inclusions in quartz from productive mpa in ore occurrence Braikovitza.

same isotope ratios for galena from lead-zinc mineralisation and from quartz-fluorite one are 18.664, 15.680, 38.815 and 18.683, 15.661, 38.813 (Amov et al., 1993).

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### REFERENCES

- Amov, B., B. Kolkovski, R. Dimitrov. 1993. Genesis and age of hydrothermal ore mineralisation in the Rhodope metallogenic zone on the basis of the isotopic composition of lead in galena.— Ann. de l 'Univ. de Sofia ,,St. Kl. Ohridski", Fac. de geologie et geogr., 85, v. 1 - Geol., 73-98 (In Bulgarian).
- Dimitrov, R. 1988. Metallogenic zonation of Bulgaria and leadzinc ore formations.– In: Lead-zinc deposits in Bulgaria, Sofia, Technica, 13-28 (In Bulgarian).
- Gadjeva, T. 1972. Aikinite from Laki deposit, the Rhodopes.-Rev. Bulg. Geol. Soc., vol. 33, 2, 257-260 (In Bulgarian).
- Ivanov, Z., B. Kolkovski, D. Dimov, S. Sarov, S. Dobrev. 2000. Structure, Alpine evolution and mineralizations of the Central Rhodopes Area (South Bulgaria).— ABCD-GEODE 2000 Workshop, Borovets, Bulgaria, Guide to exc. B, Sofia, 50 p.
- Krasteva, M., T. Todorov, 1986. Mineral-thermometric investigation of sulphide-fluorite deposit Yugovo, Central

Rhodopes.- Geoch., miner. and petrol., 22, 54-63 (In Bulgarian).

- Maneva, B., D. Manev, L. Naphtali, O. Malinov. 1989. Formational analysis as a basis of metallogenic subdivision in part of the Rhodope area. – *Geologica Rhodopica*, Sofia, *Univ. Press, v. 1*, 491-503
- Nedialkov, R., B. Maneva, L. Nikova. 1998. Granitoidic magmatism in Laki and Yugovsko Hantche area.– Ann. de I 'Univ. de Sofia ,,St. Kliment Ohridski", Fac. de geol. et geogr., v. 1 – Geologie, 90, 163-198 (In Bulgarian).
- Stoynova, M. 1988. Laki ore field.– In: Lead-zinc deposits in Bulgaria, Sofia, Technika, 79-89 (in Bulgarian).

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- Stoynova, M., Begizov, V. 1982. Bismuth minerals from Laki ore field (Northern Rhodopes).– Bull. Institutes High. Edu. "Geology and Prospecting", 10, 69-74 (In Russian).
- Stoynova, M., S. Stoynov, I. Bedrinov, M. Tokmakchieva. 1984. Magmatism and ore-formation at Laky ore field (northern Rhodopes).– *Proc. 6 IAGOD Symp.*, Stuttgart, Germany, 457-461.
- Todorov, T., 1989. Fluorite.– In: Nonmetal resources of Bulgaria. vol. 2 – Endogenous industrial minerals and rocks. Sofia, Technika, 178-196 (in Bulgarian).
- Vaughan, D. J., J. R. Craig. 1978. Mineral chemistry of metal sulfides.– *Cambridge Univ. Press*, Cambridge, 580 p.