

SILVER AND SILVER-BEARING PHASES FROM CHALA AND PCHELOIAD DEPOSITS (EASTERN RHODOPE) AND ENIOVCHE DEPOSIT (CENTRAL RHODOPE)

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ABSTRACT

Samples from Pb-Zn mineralisations in the three deposits are studied to establish the form of silver and other trace elements in them. Ag and Ag-bearing minerals such as acanthite, Te-acanthite, freibergite, Zn-freibergite, Ag-Zn-tennantite, pearceite, Te-pearceite, cervelleite (?) and mineral phase with composition $(\text{Cu}_{1.75}\text{Ag}_{1.29}\text{Zn}_{0.26})_{3.30}(\text{Sb}_{0.44}\text{Te}_{0.33})_{0.77}\text{S}_{2.93}$ nominated as "mineral A" are found. Ag is established as well in isomorphic form in galena and also in secondary copper minerals (probably as fine admixture of acanthite). New for the deposits are pearceite $[(\text{Ag}_{11.41}\text{Cu}_{4.12}\text{Fe}_{1.01})_{16.54}\text{As}_{1.47}\text{S}_{11.00}]$ and Te-pearceite $[(\text{Ag}_{11.32}\text{Cu}_{4.09}\text{Fe}_{0.65})_{16.06}(\text{As}_{1.68}\text{Sb}_{0.13})_{1.81}(\text{S}_{10.95}\text{Te}_{0.18})_{11.13}]$. Final diagnostics of cervelleite(?) and "mineral A" needs additional studies.

Key words: Pb-Zn deposits, trace elements, Ag and Ag-bearing minerals.

INTRODUCTION

Object of this study is the form of occurrence of silver in economic parageneses in the three deposits. The problem of Ag distribution in lead-zinc ores in the Rhodope deposits is discussed in several papers published until now (Breskovska et al., 1984; Kolkovski and Manev, 1988; Bonev and Neykov, 1990; etc.), but not many data are available for the deposits included in the present study. This problem is important not only for clarifying the geochemical development of ore-bearing systems, but also from practical point of view, due to its impact on the optimisation of mineral dressing processes and extracting silver from ores as additional economic component.

MATERIALS AND METHODS

The study is based on 35 ore samples located as follows: Eniovche (20), Pcheloiad (10) and Chala (5). 40 polished sections were prepared from the samples and were studied by through NU-2 and Amplival pol-U microscope at magnifications x 64 and up to 900. Photos were taken by digital Panasonic CCD colour camera model GP KR22, and images were processed through software Matrox Rainbow Runner Studio, iPhoto Express, Photoshop 5.0. Electron microprobe analyses were done by means of JEOL JSM 35 CF (Tracor Northern TH 2000) with EDEX system using JEOL standards in the laboratory of EUROTEST Plc., Sofia.

GEOLOGICAL SETTING

Eniovche deposit is a typical representative of Pb-Zn deposits, related to the Central Rhodope Dome (Ivanov et al., 2000). Due to its setting far from other deposits, it has been described as a separate one, not related to any ore field. In

some publications Eniovche deposit is considered as a part of Nedelino ore field (Bogdanov, 1959, etc.). The ore bodies are steep veins with orientation WNW, cross-cutting metamorphic rocks (Fig. 1). There are also metasomatic replacement ore bodies in distal skarns, formed in marble layers.

Pcheloiad and Chala deposits belong to Zvezdel-Pcheloiad and Spahievo ore fields, respectively. Both fields are situated in the Eastern Rhodope Paleogene depression (Fig. 1) and are related to Paleogene volcano-plutonic centres. The ore bodies represent veins with subequatorial direction and fill radial faults (Breskovska and Gergelchev, 1988; Maneva, 1988; etc.). The host rocks of the Pb-Zn mineralisation belong to the Paleogene volcano-sedimentary complex.

MINERALOGICAL CHARACTERISTICS OF SILVER AND SILVER-BEARING PHASES

Eniovche deposit

Samples from Eniovche deposit are from vein type mineralisation (level 200) and also from metasomatic replacement ore bodies (levels 550-600). Silver and silver-bearing phases are better developed in metasomatic replacement ores from the eastern flank of the deposit.

Acanthite. In the present study, compositions within the system Ag – S are nominated as acanthite. No measurements are available for the temperature conditions for the association in which these compositions are found and it is difficult to strictly confirm whether the phase observed was argentite or acanthite because both minerals are isochemical. The suggestion for primary formation of argentite is based on the presence of chalcopyrite, sphalerite and other sulphides usually formed above 200° C, as well on the minor distribution of alteration processes affecting these minerals. The stability of argentite is above 192° and phases observed in polished

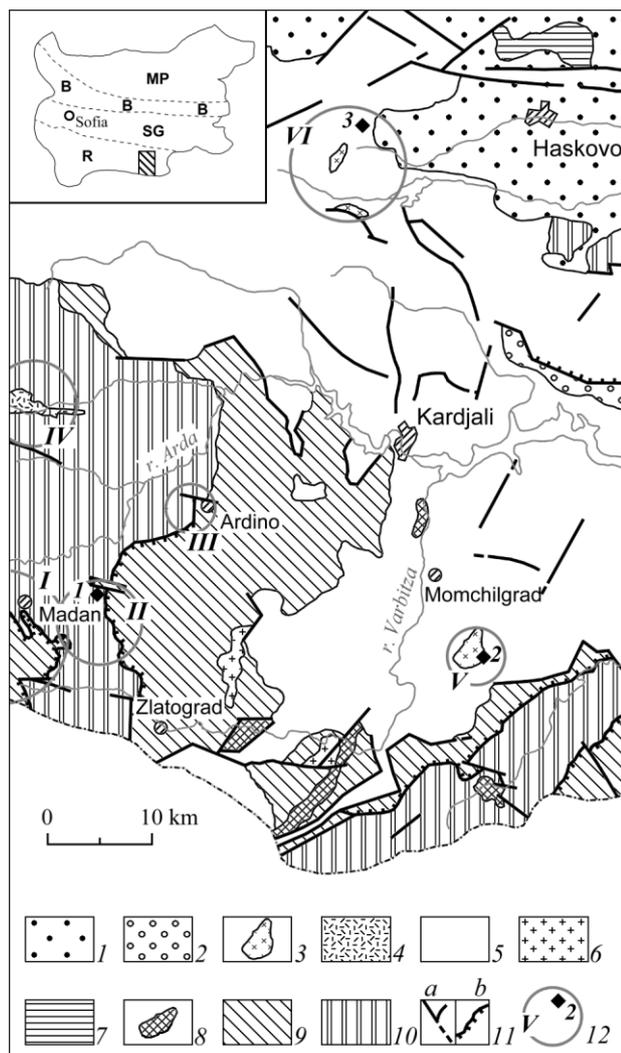


Figure 1. Schematic geological map, showing location of studied deposits (after GEOLOGICAL MAP OF P.R. BULGARIA, 1989; METALLOGENIC MAP OF BULGARIA, 1989).

Abbreviations on inset map: MP – Moesian Plate; B – Balkanides; SG – Srednogorie Zone; R – Rhodopes.

1. Neogene terrigenous sediments; 2. Paleogene molasse; 3. hypabyssal intrusive rock; 4. subvolcanic rhyolite bodies; 5. Eocene-Oligocene sedimentary, volcano-sedimentary and volcanic rocks (Eastern Rhodope depression); 6. Upper Cretaceous granitoids; 7. Triassic sandstone, schist, marble; 8. serpentinite; 9. Rhodopian Supergroup (schist, gneiss, marble, amphibolite, etc.); 10. Prarhodopian Supergroup (gneiss, gneiss-schist, amphibolite, migmatite, etc.); 11. faults (a), thrust and nappe (b); 12. base-metal ore fields and deposits studied: **I** – Madan ore field, **II** – Nedelino ore field (**1-Eniovche deposit**), **III** – Ardino ore field, **IV** – Davidkovo ore field, **V** – Zvezdel-Pcheloiad ore field (**2-Pcheloiad deposit**), **VI** – Spahievo ore field (**3-Chala deposit**).

sections should be acanthite. Acanthite grains are found among chalcopyrite as well expressed rims ($20 \times 100 \approx 200 \mu\text{m}$), build up of single grains and located along the contacts between chalcopyrite, ankerite and Mn-calcite (Plate A), or as larger grains ($50\text{--}200 \mu\text{m}$) in chalcopyrite near the contact with pyrite. Microprobe analyses established minor presence of

Cu and Fe (Table 1, No 1, 2, 3), which is probably due to the influence of the chalcopyrite matrix.

A fine isometric aggregate containing Ag, Te, Cu, $S \pm Sb$ ($10 \times 15 \mu\text{m}$) is observed in galena near the contact with pyrite. It is composed of three or four different phases with minor size and closely integrated which do not allow their precise determination. The high Ag content in the aggregate additionally complicates their determination, because of possible photocorrosional effects expected.

Freibergite is observed as fine isometric inclusions in galena, or as grains in association with tennantite, close to contact of galena with chalcopyrite (Plate B). The colour of both minerals is light grey and in reflected light they are hardly distinguished, but through SEM the difference is well visible (inset on Plate B). Microprobe analyses determine Ag content about 12 wt % and the phase could be nominated as Ag variety of tetrahedrite, known as freibergite (according to Mozgova and Tzegin, 1983, Chvileva et al. 1988). Zn content in some of the analysed grains is up to 6 wt. % and they could be nominated as *Zn freibergite*. (Table 1, No 4, and 5).

Ag-bearing Zn tennantite is found as fine oval grains up to $10\text{--}30 \mu\text{m}$ along the contacts between sphalerite and galena or in association with chalcocite. The absence of Sb determines it as end-member in tennantite-tetrahedrite row and increasing content of Zn (up to 10.61 wt. %) nominates it as Zn variety of tennantite. Silver content is not high (to 0.27 wt. %), but remains constant within the grains (Table 1, No 6, 7).

Cervelleite (?) is an extremely rare Ag mineral found for the first time in abandoned Bambolla Mine (previously known as Moctezuma tellurium deposit), Sonora, Mexico (Criddle et al. 1989) as thin rim around acanthite and hessite in association with native silver, benleonardite, pyrite and sphalerite. The mineral is tellurium analogue of aguilarite. Cervelleite-like mineral was described by Helmy (1999) in Precambrian Ag-rich volcanogenic Zn-Cu-Pb deposit Um Samiuki (Eastern Desert, Egypt). Two varieties of the described mineral are discussed in this deposit – a Cu-rich one (Cu up to 6 wt. %) and the other containing <0.25 wt. % copper.

Findings of similar minerals were described as “unnamed mineral” by Gadjeva (1983, 1985) in Shadiitza (Nedelino ore field, Central Rhodopes). Later Bonev and Neykov (1990) and Bonev (1991) described a mineral with very similar composition to that mentioned by Gadjeva (1985) in the Pb-Zn Ardino deposit. Ag_4TeS phase is found by Marinova and Kolkovski (1994) in Belevsko deposit (Davidkovo ore field, Central Rhodopes). In all these findings there is also a very broad range of copper content from 3.3 wt. % (Gadjeva, 1985) up to 18.17 wt. % (Marinova and Kolkovski, 1994). Analysis of the available data shows that variations of copper content in this phase is due to the possibility of replacement position of silver by copper. As a rule, the described grains are very fine and photocorrosional effects additionally cause difficulties for precise diagnostics of the phases found.

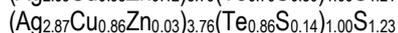
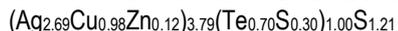
Cervelleite (?) in Eniovche deposit was first reported by Dobrev (2001). It is developed in the central part of a large

Table 1. Microprobe analyses of Ag and Ag-bearing phases

No	Sample No	mpr. an. No	Mineral phase	Element content [wt. %]									Formula	
				Ag	Cu	Zn	Fe	As	Sb	Te	S	Σ		
Eniovoche deposit														
1	9	4	acnt	82.89	-	-	-	-	-	-	-	16.72	99.61	Ag _{1.79} S _{1.21}
2	9	5	acnt	84.02	1.77	-	-	-	-	-	-	14.66	100.45	(Ag _{1.85} Cu _{0.07}) _{1.92} S _{1.08}
3	9	7	acnt	84.76	1.29	-	0.24	-	-	-	-	12.78	99.07	(Ag _{1.95} Cu _{0.05} Fe _{0.01}) _{2.01} S _{0.99}
4	13	14	Zn frbg	17.96	27.05	4.59	-	-	25.44	-	-	24.55	99.59	(Cu _{7.55} Ag _{2.94} Zn _{1.24}) _{11.73} Sb _{3.70} S _{13.57}
5	18	25	Zn frbg	12.01	27.66	6.11	0.14	1.24	28.95	-	-	23.61	99.72	(Cu _{7.73} Ag _{1.97} Zn _{1.65} Fe _{0.04}) _{11.39} (Sb _{4.22} As _{0.29}) _{4.51} S _{13.08}
6	12	8	Ag-bear. Zn ten	0.27	40.91	9.54	1.31	16.94	1.38	-	-	29.12	99.47	(Cu _{9.52} Ag _{0.04} Zn _{2.16} Fe _{0.35}) _{12.07} (As _{3.34} Sb _{0.17}) _{3.51} S _{13.43}
7	6	24	Ag-bear. Zn ten	0.15	41.95	10.61	0.93	17.93	-	-	-	28.40	99.97	(Cu _{9.74} Ag _{0.02} Zn _{2.39} Fe _{0.25}) _{12.40} As _{3.53} S _{13.07}
8	13	10	cerv(?)	58.15	12.51	1.55	-	-	-	17.85	9.71	99.77	(Ag _{2.69} Cu _{0.98} Zn _{0.12}) _{3.79} (Te _{0.70} S _{0.30}) _{1.00} S _{1.21}	
9	13	11	cerv(?)	59.70	10.52	0.42	-	-	-	21.15	8.45	100.24	(Ag _{2.87} Cu _{0.86} Zn _{0.03}) _{3.76} (Te _{0.86} S _{0.14}) _{1.00} S _{1.23}	
10	13	12	min. A	30.16	24.03	3.71	-	-	11.63	8.96	20.32	98.81	(Cu _{1.75} Ag _{1.29} Zn _{0.26}) _{3.30} (Sb _{0.44} Te _{0.33}) _{0.77} S _{2.93}	
Pcheloiad deposit														
11	30	36	prc	60.94	12.96	-	2.80	5.45	-	-	-	17.46	99.61	(Ag _{11.41} Cu _{4.12} Fe _{1.01}) _{16.54} As _{1.47} S _{11.00}
12	30	35	Te-bear. prc	59.75	12.72	-	1.77	6.16	0.74	1.16	17.18	99.48	(Ag _{11.32} Cu _{4.09} Fe _{0.65}) _{16.06} (As _{1.68} Sb _{0.13}) _{1.81} (S _{10.95} Te _{0.18}) _{11.13}	
13	25	19	(Ag,Te) Zn tetr	0.26	37.04	5.51	0.38	3.25	27.63	0.30	25.29	99.66	(Cu _{9.73} Ag _{0.04} Zn _{1.41} Fe _{0.11}) _{11.29} (Sb _{3.78} As _{0.72}) _{4.50} (S _{13.16} Te _{0.04}) _{13.20}	
14	25	21	(Ag) Zn ten-tetr	0.55	40.83	8.81	0.39	12.84	9.01	-	27.43	99.86	(Cu _{9.86} Ag _{0.08} Zn _{2.07} Fe _{0.11}) _{12.12} (As _{2.63} Sb _{1.14}) _{3.77} S _{13.12}	
15	26	28	Ag Zn ten-tetr	7.13	35.55	9.73	0.40	5.48	15.99	-	25.83	100.11	(Cu _{9.05} Ag _{1.07} Zn _{2.40} Fe _{0.11}) _{12.63} (Sb _{2.13} As _{1.17}) _{3.30} S _{13.04}	
16	26	29	Ag Zn tetr	7.79	37.03	6.48	0.44	4.32	18.90	-	24.37	99.33	(Cu _{9.74} Ag _{1.21} Zn _{1.65} Fe _{0.13}) _{12.73} (Sb _{2.60} As _{0.96}) _{3.56} S _{12.71}	
Chala deposit														
17	32	32	(Te) acnt	88.69	-	-	-	-	-	1.55	9.41	99.65	Ag _{2.19} (S _{0.78} Te _{0.03}) _{0.81}	
18	31	22	(Ag) enrg	1.55	46.14	-	2.15	16.26	-	-	33.11	99.21	(Cu _{2.86} Ag _{0.06} Fe _{0.15}) _{3.07} As _{0.86} S _{4.07}	
19	31	23	(Ag) enrg	0.68	48.08	-	1.61	17.54	-	-	32.66	100.57	(Cu _{2.96} Ag _{0.02} Fe _{0.11}) _{3.09} As _{0.92} S _{3.99}	
20	32	31	(Ag) enrg	1.25	46.53	-	1.62	16.84	-	-	32.92	99.16	(Cu _{2.89} Ag _{0.05} Fe _{0.11}) _{3.05} As _{0.89} S _{4.06}	
21	34	34	(Ag) enrg	0.32	46.41	-	2.23	17.26	-	-	32.93	99.15	(Cu _{2.88} Ag _{0.01} Fe _{0.16}) _{3.05} As _{0.91} S _{4.05}	
22	32	30	Ag cov(?)	10.85	55.86	-	0.77	2.08	-	-	29.99	99.55	mixture	
23	34	33	2500 μm ²	9.86	48.57	0.20	5.60	5.24	-	-	31.27	100.74	mixture	

Abbreviations: **Ag-bear.**=(Ag) – Ag-bearing; **Te-bear.**=(Te) – Te-bearing; **ten** – tennantite; **acnt** – acanthite; **frbg** – freibergite; **cerv** – cervelleite; **min. A** – mineral A (formula calculated as skinnerite); **prc** – pearceite; **ten-tetr** – tennantite-tetrahedrite; **enrg** – enargite; **cov** – covellite, **mpr. an.** – microprobe analysis

galena aggregate (Plate C) as irregular grains. In reflected light it is grey with slight greenish shade. Its reflectivity is relatively high, but 3 – 5% lower, compared with galena. The mineral phase is isotropic. Two quantitative analyses (Table 1, No 8, 9) establish components that are very close to the discussed above. The stoichiometric formula are as follows:



Mineral A is found as a thin rim several microns thick around cervelleite (?) (Plates C, D). In reflected light it is grey but darker, compared with cervelleite (?) and its reflectivity is lower compared with cervelleite and galena (probably about 30%). Minor size of the mineral does not allow distinct observation of anisotropic effects typical for it. Microprobe analysis (Table 1, No 10) established composition similar to goldfieldite and freibergite but stoichiometric estimations lead to formula much closer to skinnerite (Karup-Moller and Makovicky, 1974) with

some deficit in the cation part and distinctly higher silver content: $(\text{Cu}_{1.75}\text{Ag}_{1.29}\text{Zn}_{0.26})_{3.30}(\text{Sb}_{0.44}\text{Te}_{0.33})_{0.77}\text{S}_{2.93}$. It is possible that the analysed phase has an intermediate composition between goldfieldite, skinnerite and pyrargirite or a mixture between them, which could be hardly distinguished at the magnifications used. Outside of the contour marked by skinnerite, there is another mineral grain with elongated shape, the optical features of which are similar to those described for the last two minerals. Microprobe analyses established contents of Ag, Te, Cu and Sb, but its minor size does not allow precise determination of its stoichiometry. It is possible this phase to be very fine intergrowth between mineral A and cervelleite (?).

The most common Ag-bearing phases are members of the tennantite-tetrahedrite row. They demonstrate a broad range of trace elements presence especially Ag, Zn and Te in them.

Pcheloiad deposit

Samples from Pcheloiad deposit are from ore zones 2 and 14 (level 490) and adit 56.

Pearceite is found in samples in association with chalcopyrite and pyrite. It is observed as fine irregular inclusions in chalcopyrite along the contact with pyrite (Plate E). The colour in reflected light is light grey but due to the minor size (20–30 µm) of its grains the anisotropic effects typical for this mineral are not distinctly observed. Microprobe analyses established increased content of Te and Sb in some grains (Table 1, No 11, 12) which are common trace-elements in the pearceite-polybasite group. The crystallochemical formula of pearceite with content of Te is:



and the phase should be nominated as *Te-bearing pearceite*.

Ag-tennantite-tetrahedrite is relatively frequently found in galena-sphalerite association. They form thin veinlets in sphalerite or irregular isometric and slightly rounded grains along the contact between sphalerite and pyrite or chalcopyrite. Rarely phases associate with secondary covellite developed over chalcopyrite, or they form thin veinlets together with chalcopyrite cutting sphalerite. Some of the grains are often up to 200–300 µm or even to 2 – 3 mm and analyses established higher content of silver in them. The chemical composition of some analysed grains is characterised with increased content of Zn and presence of Te (Table 1, No 13 – 16). Silver content in some of them is up to 7–8 wt. %, but it is not enough to classify them as freibergite (according to the classification of Chvileva et al., 1988). In cases when Sb dominates over As, the phases are represented by intermediate members closer to tetrahedrite and they are nominated as *Ag-Zn tetrahedrite*. Crystallochemical formulas of the analysed grains from the tennantite-tetrahedrite mineral row are given in Table 1.

Chala deposit

Samples from Chala deposit are from level 474.

Te-acanthite is found as fine isometric grains along the contact between bornite and Ag-enargite. Their colour is lighter but in the reflected light microscope they could be hardly distinguished. Observation in the scanning electron microscope allows distinct observation of their differences, compared with the other neighbour minerals. Chemical composition obtained through quantitative microprobe analysis determines it as acanthite and presence of Te (1.55 wt. %) nominates it as *Te-bearing acanthite* (Table 1, No 17, Plate H).

Ag-bearing enargite. Inclusions of this mineral are observed among chalcopyrite aggregates (Plate F), often in association with idiomorphic pyrite. They are quadrangle, elongated or irregular in shape and their size is 40–100 µm. In some cases the mineral forms a rim or fine aggregates over corroded quartz along the contact with chalcopyrite. Elongated enargite-galena aggregates (about 130 µm) or single elongated enargite grains (70 µm long) in galena are developed as well. Enargite also forms fine intergrowths with other sulphides (Plate G). Enargite is isochemical with luzonite and here it is determined on the base of the differences of the optical properties of both

minerals. The content of Ag in it is comparatively low, so the mineral phase could be nominated as *Ag-bearing enargite* (Table 1, No 18-21).

Ag-bearing covellite is developed over primary chalcopyrite and tennantite in association with bornite and chalcocite. It is characterised by inhomogeneous texture and contains numerous sectors with light grey colour. Such sectors are quite distinctly distinguished, when observed in COMPO regime of the scanning electron microscope (Plate H). They probably reflect very close intergrowths between covellite and Te-bearing acanthite (?) and this is the reason for higher Ag content (over 10 wt. %) registered in the analysis (Table 1, No 22).

The higher Ag content in the observed association of secondary copper minerals is confirmed by area quantitative microprobe analysis covering about 2 500 µm² in the central part of an aggregate and it registered about 10 wt. % of Ag (Table 1, No 23). Different mineral phases could not be distinguished because of the very close intergrowth relations between them, but the analysis draw the attention to copper mineralisation in this deposit as possible carrier of a part of silver in it.

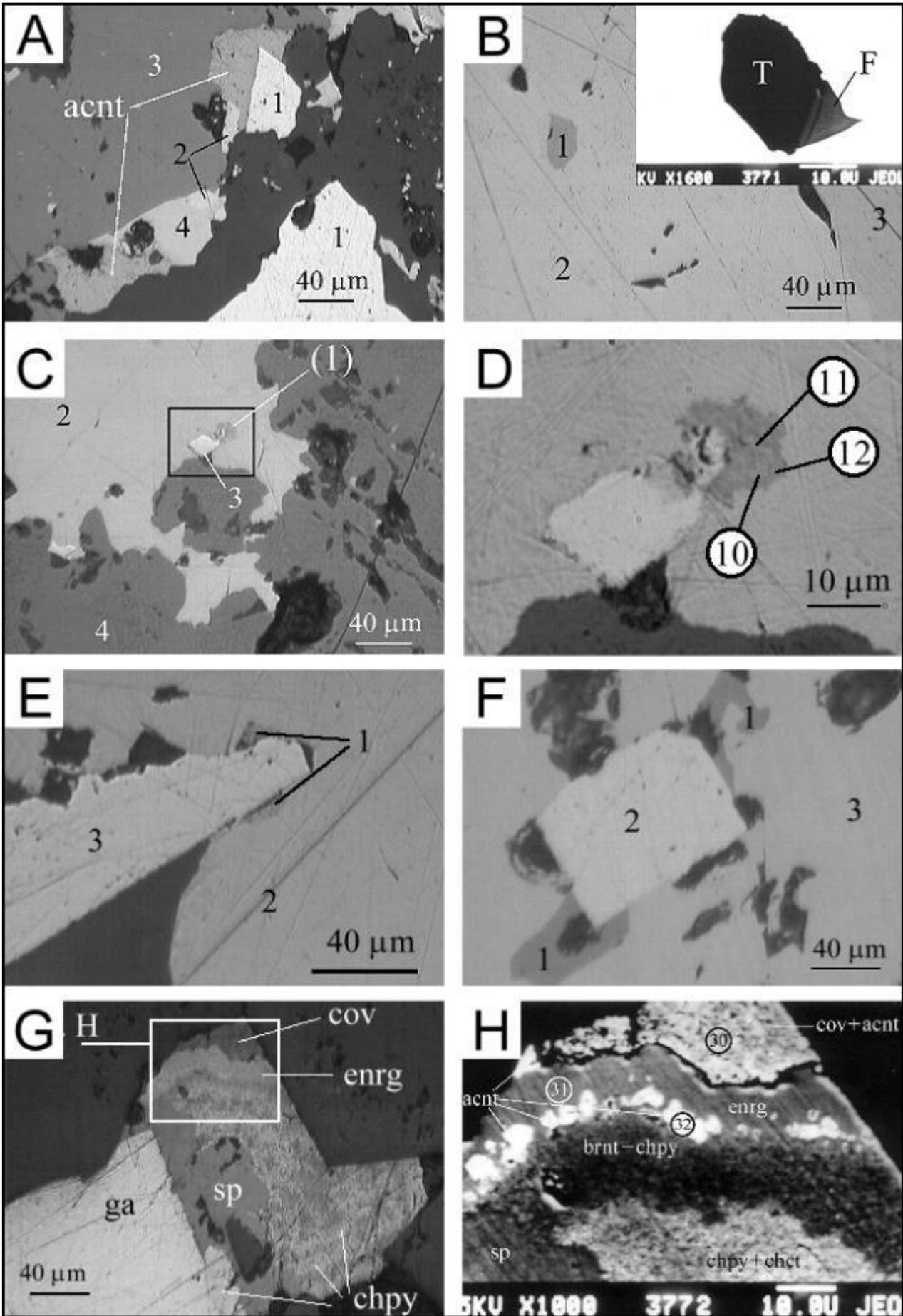
CONCLUSIONS

The results from the present study suggest that galena in the three deposits associates with mineral microinclusions of silver and silver-bearing minerals such as acanthite, freibergite, Ag-bearing Zn tennantite, cervelleite (?) (Eniovche deposit), pearceite, Te-bearing pearceite, Ag – tennantite-tetrahedrite (Pcheloiad deposit), Te-acanthite, Ag-bearing enargite, Ag-bearing covellite (Chala deposit). ICP analyses of galena monomineral probes registered silver in a broad range (from traces to 138 ppm) but in most cases the studied galena contains microinclusions of Ag-bearing minerals that could not be separated during the preparation of monomineral probes and it is not possible to distinguish the ratio between isomorphic presence of silver in galena and its presence as single silver-bearing mineral phases in it.

Samples from metasomatic ore bodies in Eniovche deposit contain various types of Ag and Ag-bearing minerals compared with those from the vein part of the deposit. This could be explained with development of re-mobilisation and re-distribution processes.

The most frequently found silver bearing phases in Pcheloiad deposits are phases from the tennantite-tetrahedrite mineral row developed along the contacts between galena and chalcopyrite. It should be mentioned that in most cases phases closer to the tetrahedrite end member contain more silver compared with the tennantite members of the mineral row.

Ag-tennantite-tetrahedrite commonly form visible grains among galena, chalcopyrite and sphalerite. Pearceite and Te-bearing pearceite are also found in this deposit. Silver content in galena as isomorphic element is relatively low.



Plates

Plate A. deposit Eniovche. Acanthite (acnt) developed along the boundary of sulphide minerals. (pyrite – 1, galena – 2, sphalerite – 3, dark grey – gangue mineral) – *Refl. light N II*.

Plate B. deposit Eniovche. Inclusion of tennantite and freibergite (1) in galena (2) near the contact with chalcopyrite (3). Tennantite and freibergite could not be distinguished in reflected light. Right corner top – fragment from Plate 2 performed through SEM (Backscattered electron image, COMPO regime). Tennantite – (T), freibergite – (F).

Plate C. deposit Eniovche. Aggregate set up by cervelleite (?) and mineral "A" (in quadrangle) along on the contact between galena (2) and pyrite (3), (4) – sphalerite, dark grey – gangue. – *Refl. light N II*.

Plate D. Fragment from Plate C. Ciphers in the circles – No of microprobe analysis.

Plate E. deposit Pcheloiad. Pearceite (1) along the contact between chalcopyrite (2) and pyrite (3). – *Refl. light N II*.

Plate F. deposit Chala. Ag-bearing enargite (1) along euhedral pyrite crystal (2) among chalcopyrite (3). – *Refl. light N II*.

Plate G. deposit Chala. Sphalerite-chalcopyrite-enargite aggregate (sp, chpy, enrg) on a boundary of galena grain (ga) with quartz. Secondary copper minerals are well established (covellite – cov, chalcocite – chct, bornite – brnt). – *Refl. light N II*.

Plate H. A fragment from Plate G. Covellite-enargite-chalcopyrite-bornite-chalcocite-sphalerite aggregate with acanthite. Ciphers in circles show location and No of microprobe analysis. – *Backscattered electron image, COMPO regime*.

Typical for Chala deposit is a relation between Ag-bearing phases and secondary copper minerals such as covellite. A very fine mixture of secondary copper minerals and Ag-bearing minerals forms aggregates up to several mm. Te-bearing acanthite and Ag-bearing enargite are other minerals that carry silver in this deposit. During ore dressing, part of Ag-bearing minerals, closely associating with copper minerals, may be lost.

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