

GOLD IN COPPER DEPOSITS FROM THE SREDNOGORIE ZONE (BULGARIA)

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ABSTRACT

Au-Ag phases from three types of deposits in the Srednogorie zone are studied - Chelopech (massive copper-pyritic formation), Elatzite and Medet (porphyry-copper formation) and Zidarovo and Rossen (vein copper formation). Two morphological types of Au-Ag phases are established in these deposits - finegrained (1-70 mkm) and coarsegrained (>70 mkm), first of which has a dominate distribution. The paper discussed their geochemical and morphological features, position in the ore forming processes comparing the similarities and differences of their distribution in the mentioned deposits, as well.

INTRODUCTION

Au and Ag are two elements occurring constantly in small quantities in the copper deposits from the Srednogorie zone (Bulgaria). These deposits are the main sources of gold obtained as a by-product from the copper concentrates through metallurgical processing. This is the reason why, the study of the distribution, morphology, chemical composition and other features of Au-Ag phases is very important, not only for investigations of the ore-forming processes in these deposits, but also for the optimization of their extraction.

The analytical examinations were made over samples from type deposits chosen (Fig. 1), as follows:

- Chelopech (massive copper-pyritic formation);
- Medet and Elatzite (porphyry-copper formation);
- Zidarovo and Rossen (vein copper formation).

The material was collected during the last 10 - 15 years, so representative samples from different levels in the deposits were guaranteed.

Some of the latest studies on the form of Au-Ag presence in copper deposits suggest, that three main types (on the basis of their size) can be distinguished (Zelenov, 1989). They were determined as coarsegrained (>70 mkm), finegrained (70-1 mkm) and finelydispersed (<1 mkm) phases. Such a classification is based mainly on the behavior of Au-Ag phases during the technological operations in the beneficiation of copper ores and it is suitable from a practical point of view. The objects of this study are the first and the second type. Several attempts, including electron microscopy (magnification over 6000x), were made, but Au-Ag phases sized less than 1 mkm were not found in the samples studied.

Other gold-bearing minerals previously established in some deposits (e.g. kostovite, nagiagite, sylvanite from Chelopech, Tersiev, 1968) have a very

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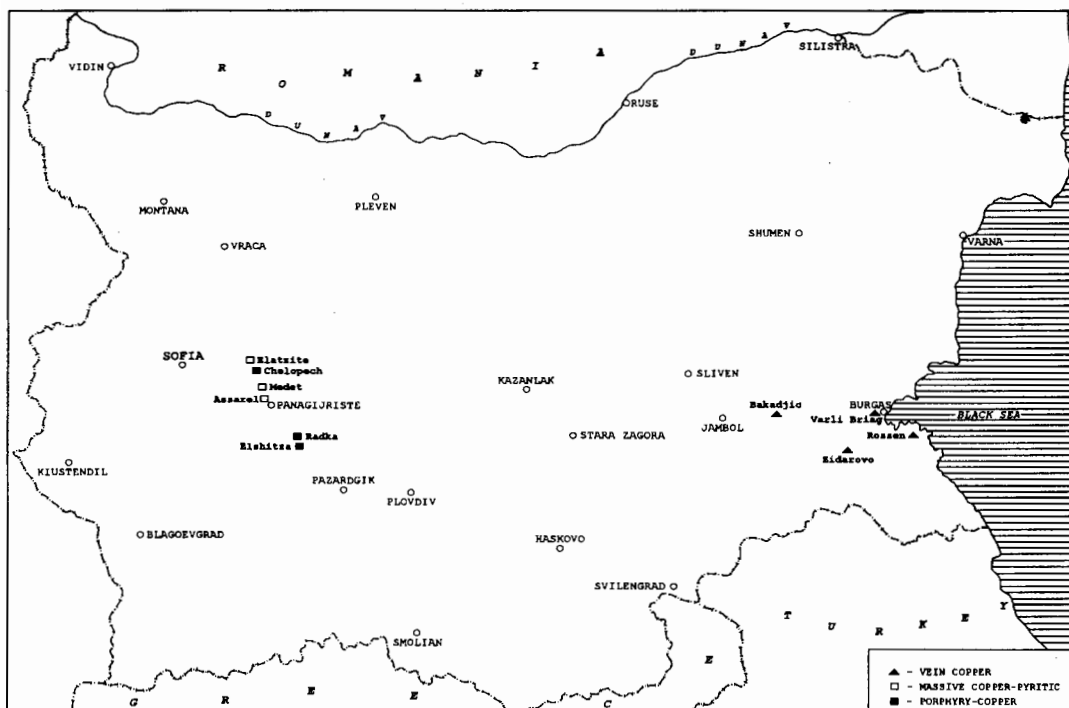


Fig. 1: Types of deposits

rare distribution in copper ores, so they are not included in this study.

AU-AG PHASES IN THE MASSIVE COPPER-PYRITIC DEPOSITS

The massive copper-pyritic deposits are commonly characterized by a larger spreading of Au-Ag phases in comparison to the two other types of copper deposits in the Srednogorie zone. Several deposits of this type (Chelopech, Elshitz, Radka) are known in the central part of the Srednogorie zone and the Chelopech deposit is the most significant among them with its gold content.

Gold-bearing phases in this deposit were described for the first time by Tersiev (1968). Later, new data and determination of two different morphological types of Au-Ag phases were published by Kovachev et al. (1988). These two types are finegrained Au-Ag phases in association with sulfides and sulphosalts, and coarsegrained phases associating with anillite, digenite, bornite and barite.

The first type was observed in enargite veinlets cutting through pyrite, which has a significant content of copper (up to 1 wt. %). The Au-Ag grains are between 5 - 20 mkm in size and optically they look homogeneous. Microprobe analyses, however, established that they have a distinct zonal texture. The core of the grains contains Ag and Cu between 2 and 3 wt. %, but the content of Cu increases extremely up to 16 wt. % in the rim of some grains (Table 1). A slight increase in of Ag and presence of Fe (about 1 wt. %) was also found in the rim zone. The absence of As-lines in the spectrum analyzed, cancels the possibility of borrowing Cu and Fe from the enargite matrix.

The coarsegrained Au-Ag phases were found in depth - level 700 under the daylight surface. The findings were localized in the northern periphery of the copper-pyritic body in the range of a sheer tectonised zone with E-W direction.

Table 1: Chemical composition of Au-Ag phases from the Chelopez ore field by electron microprobe analyses (in weight %)

| Mineral association | Au | Ag | Cu | Fe | Tl |
|--|-------|------|-------|------|------|
| Finegrained Au-Ag phases in tennantite | 95,14 | 2,87 | 1,98 | - | - |
| | 94,82 | 3,46 | 1,71 | - | - |
| | 87,67 | 4,26 | 7,63 | 0,44 | - |
| | 79,35 | 3,43 | 16,02 | 1,20 | - |
| | 92,77 | 3,83 | 3,29 | 0,11 | - |
| | 93,77 | 2,78 | 2,88 | 0,57 | - |
| | 94,85 | 4,27 | - | 0,88 | - |
| | 95,45 | 4,33 | - | 0,22 | - |
| 95,86 | 3,71 | - | 0,43 | - | |
| Coarsegrained Au-Ag phases with anillite and other Cu-sulfides | 96,27 | 3,73 | - | - | - |
| | 95,06 | 4,94 | - | - | - |
| Coarsegrained Au-Ag phases with chalcopyrite, bornite and pyrite | 97,69 | 2,19 | - | - | 0,13 |
| | 92,84 | 7,16 | - | - | - |
| | 98,11 | 1,89 | - | - | - |
| | 96,34 | 3,31 | - | - | 0,35 |

The host rocks are quartzitized andesitic tuffs with evident traces of leaching the rockforming and ore minerals. The probable reason of this intensive leaching is the active hydrothermal metamorphic processes which look place during the ore-formation. The Au-Ag aggregates have an average size of 2 mm and their forms are usually isometric, botroidal or irregular. They fill up pores in the rocks, but sometimes they have free surface, which is rough or marked by regular ribbons. Hypidiomorphic and xenomorphic texture could be seen after a texture corrosion over the aggregates.

The silver content varies from 1.32 to 8.52 wt.% in the aggregates, but it is a constant within a single grain. The distribution of Ag contents (based on 39 microprobe analyses) is characterized by two peaks at 3.73 wt.% and 4.94 wt.%. About 44 % of the analyzed grains are close to the range of the first peak and about 28 % - to the second one. A direct correlation exists between Au and Ag in the ore body, where coarsegrained aggregates were found. The coefficient of linear correlation is 0.6358 and the level of significance is 0.5751 (probability - 0.995, 19 analyses). The relations between the contents of Au and Ag, reduced to the local geochemical background, show that Ag occurs also as other silver-bearing minerals, in spite of the significant space correlation between these two elements. The X-ray patterns of Au-Ag phase from Chelopez are very close to that of native gold and the parameter of the unit cell ($a_0 = 4.080 \text{ \AA}$) is a little larger than the standard one.

The existing data could indicate that re-crystallization is the main process, resulting in the formation of coarsegrained aggregates of Au-Ag phases. It should be taken into consideration, that Au is characterized by comparatively good solubility as it is one of the hydrophilic elements (Smith, 1968) and a its multiple redistribution is possible to take place within one ore-forming process. On the basis of experimental studies, it was established that the solubility of Au in water under subcritical temperatures and its transportation as simple hydrocomplexes or hydrosulphide complexes is enough for the formation of industrial deposits (Levin, Zotov, 1986). This publication also shows that the maximum solubility of Au in hydrosulphide form is appr. 250°C, which is the possible temperature for re-crystallization of the

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coarsegrained Au-Ag phases in the Chelopech ore deposit. The shape of the Au distribution curve in the northern part of the section studied, exposes enrichment of gold along the fault zone, as well as its deficit is typical for the host rocks surrounding the copper ore body. The minerals in association with Au-Ag phases are free of trace elements and their composition is very close to the stoichiometric one, which could be another evidence for recrystallization processes that took place during the ore formation.

The two types of Au-Ag phases could be found also in the other massive copper-pyritic deposits from the Central Srednogorie zone. Their features were not separated distinctly in the previous studies, but the fact that there is a significant morphological difference in Au-Ag phases formed through different mineral parageneses is mentioned by Bogdanov (1987).

The finegrained Au-Ag phases are most common for the initial stages of the ore-formation in the Radka and Elshitzza ore deposits. Gold grains (1 - 50 mkm) occur as individual inclusions mainly in chalcopyrite ores, very rarely, in the interstices of pyrite.

The coarsegrained Au-Ag phases were formed later and they associate with minerals from bornite-tennantite parageneses. Their sizes vary from 50 up to 100 mkm, sometimes veinlets even to 2 cm could be found (Tokmakchieva, Velchev, 1978). Except veinlets, coarse grained gold also forms isometric aggregates or nest-like accumulations. The texture of aggregates is not homogeneous. A matrix of native gold (Ag = 1.5 - 2 wt.%) is usually banded by yellow-white layers or spots of Au-Ag phases containing from 16 to 28 wt.% Ag (Tokmakchieva, Velchev, 1978).

Summarizing the features of Au-Ag phases from all the massive copper-pyrite deposits in the Srednogorie zone, it should be noted that they were formed over a long period of mineralization during the productive ore-formation. The finegrained Au-Ag phases are more homogeneous, they contain less silver and were formed through the initial stages of mineralization in association with chalcopyrite and pyrite. The coarsegrained Au-Ag phases are characterized by larger quantities of Ag dispersed irregularly in them and they were formed at later stages of the ore-forming processes.

AU-AG PHASES IN THE PORPHYRY-COPPER DEPOSITS

Au-Ag phases have a relatively minor distribution in the porphyry-copper deposits in comparison to the massive copper-pyritic deposits. No findings of any other gold-bearing minerals, except Au-Ag phases have been reported until now. The presence of finegrained Au-Ag phases and a very rare finding of coarsegrained gold inclusions is a distinguished feature of the porphyry-copper deposits. A typical form of occurrence of Au-Ag phases in porphyry-copper deposits is small inclusions (1-30 mkm) in chalcopyrite from the most abundant pyrite-chalcopyrite association. Not so often, Au-Ag phases could be found as inclusions in pyrite or quartz from the later mineral associations. Au-Ag phases were found as an exception with hessite - Medet ore deposit or with siggenite (Elatzite ore deposit, Dimitrov, 1973); The morphology of Au-Ag phases is usually isometric (irregular shape or droplike) or elongated. The latter form mentioned is more common, when Au-Ag phases fill up fine fractures in the host sulfide minerals.

The larger part of Au-Ag phases in the Medet ore deposit associate with chalcopyrite from the main economic paragenesis. It was confirmed not only through the microscopic observations, but also by the quantitative chemical analyses of copper concentrate in which Au and Ag content is several times higher than in the pyritic and molybdenum concentrates and in the waste

products. All registered Au-Ag findings belong to the finegrained phases in the range 2 - 50 mkm. A specific distribution in their zonation was established in this deposit. Au-Ag inclusions with rounded shape are more typical of the upper part of the deposit, as well as, the irregularly shaped inclusions are more common in the deeper part of the ore body. These two morphological types differ also by their chemical composition. The first type is characterized by minor quantity of Ag (8 - 19 wt.%), whereas the inclusions from the lower part of the deposit contain Ag between 26 and 32 wt.%. There is a well expressed zonation in Ag distribution in the single inclusions from the first type, marked distinctly by a silver-rich boundary at the margin of the grains. The silver content varies from 8.21 wt.%; in the core, up to the 19.3 wt.% in the marginal part. 25 microprobe analyses (step 2 mkm) established a gradual exchange of the silver content from the core to the rim of a single grain. Such a well expressed zonation is not typical of the Au-Ag grains from the lower part of the ore body in which the Ag content is distributed irregularly.

It could be presumed that part of the silver was re-mobilized towards the end of the ore-forming processes and used to form some silver-bearing minerals (e.g. hessite) localized at the upper part of the deposit.

Au-Ag phases from the Elatzite ore deposit were observed as fine grained inclusions filling up microfractures in chalcopyrite. None were established in pyrite, although it was reported in a previous study (Tokmakchieva, 1982) that chemical analyses of monomineral pyrite probes registered traces of minor gold quantities. Minor amounts of gold were mentioned in single monomineral probes of magnetite, barite, limonite, molybdenite and calcite through chemical analyses, but no available data of their form of presence exist (Dimitrov, 1974). Tokmakchieva (1982) also reported of the presence of very small rounded grains in chalcopyrite observed through SEM (magnification 8100 - 28000), which could be classified as a finelydispersed type of gold inclusions. Our attempts to find such objects through SEM investigations were not positive and we could not confirm the presence of finelydispersed Au-Ag phases, but by all means, the problem is still open.

The usual form of finegrained inclusions in chalcopyrite are rounded or elongated and their size along the longitudinal axis is from 5 up to 40 mkm. A distinguishing feature of their chemical composition is a relatively high content of silver. This fact was marked by Dimitrov (1973) and now it was confirmed through more than 20 quantitative microprobe analyses, all of them registering Ag content in the range of 24 - 29 wt.% (Table 2). Minor amounts of Cu and Fe present constantly as trace elements in the grains analyzed.

The spatial distribution of Au-Ag phases shows preferable connection to the chalcopyrite from the central parts of the deposit.

The Asarel ore deposit differs from the Medet and Elatzite ore deposits by its relatively lower distribution of Au-Ag phases. They occur as very small inclusions (<10 mkm) which complicate their precisely diagnostics. The optical data are very close to these typical of the native gold and electrum and the presence of Au and Ag was confirmed by qualitative microprobe analyses (Petrunov et al., 1991). The higher quantity of Au-Ag phases is significant for the quartz-pyrite parageneses (Bogdanov, 1987), where two kinds of inclusions, determined as native gold and electrum by its optical features were established. Studies on the heavy nonmagnetic fraction suggested a possibility for the existence of coarsegrained Au-Ag phases in the deposit. Several quantitative chemical analyses indicated an extremely high content of gold 60 - 280 times higher than the average content (Strashimirov, 1991). These unusual contents could be explained taking into consideration a possible presence of

Table 2: Chemical composition of finegrained Au-Ag phases from the Medet (1) and Elatzite (2) ore deposits by electron microprobe analyses (in weight %)

| Mineral association | | Au | Ag | Cu | Fe |
|---------------------|---|---|-------|-------|------|
| 1 | Au-Ag phases in chalcopyrite from upper levels | 80,70 | 19,30 | - | - |
| | | 86,32 | 12,20 | - | - |
| | | 90,00 | 9,09 | - | - |
| | | 90,24 | 8,51 | - | - |
| | | 89,58 | 8,21 | - | - |
| | | 87,06 | 11,12 | - | - |
| | Au-Ag phases in chalcopyrite from deeper levels | 72,18 | 27,82 | - | - |
| | | 70,12 | 29,88 | - | - |
| | | 67,84 | 32,16 | - | - |
| | | 72,94 | 27,06 | - | - |
| | | 73,37 | 26,63 | - | - |
| | | 70,48 | 29,52 | - | - |
| | 2 | Au-Ag phases in chalcopyrite (central part of ore body) | 67,32 | 29,76 | 1,73 |
| 70,02 | | | 28,74 | 0,89 | 0,35 |
| 71,74 | | | 27,61 | 0,57 | 0,08 |
| 70,27 | | | 27,73 | 1,32 | 0,68 |
| 69,08 | | | 28,60 | 1,56 | 0,77 |
| 68,45 | | | 28,58 | 1,86 | 1,11 |
| | | 72,61 | 24,15 | 1,50 | 1,03 |

coarsegrained Au-Ag phases in some probes. Chemical analyses established also a very distinct zonation in the gold distribution in the deposit. The upper part (oxidation zone) has a relatively low gold content, as well as, the contact zone between it and the secondary sulfide mineralization zone is characterized by a constantly high gold content - usually 2 or more times above the average.

A possible correlation between the gold content and ferrooxides in the porphyry-copper deposits was presumed by Lowell (1980). This author generalized a large massive of empiric data from numerous deposits and concluded that the gold content increase in those deposits which have a higher content of magnetite and hematite. This fact is also valid for the Bulgarian porphyry-copper deposits. A significant presence of magnetite and hematite in the ores from Medet and Elatzite corresponds to the higher gold contents in comparison to that from the Asarel deposit where the two ferrooxide minerals are very rare.

AU-AG PHASES IN THE VEIN COPPER DEPOSITS

The vein type copper deposits are localized at the eastern part of the Srednogorie zone. The Zidarovo and Bacadjik ore fields are characterized by larger presence of lead and zinc, as well as, molybdenum and cobalt are typical of the Rossen ore field. The first group is distinguished by its relatively higher content of Au-Ag phases.

Two types of gold-bearing phases were observed in the Zidarovo ore field - native gold and electrum (Kovachev, 1991). The native gold forms fine veinlets or isometric inclusions in pyrite from the Cu-Bi-Te ore type. Their sizes relate them to the finegrained Au-Ag phases (usually 30-60 mkm) and the silver content varies from 8.3 to 12.6 wt.% (Table 3). The other type Au-Ag phases,

Table 3: Chemical composition of Au-Ag phases from the Zidarovo ore field by electron microprobe analyses (in wt. %)

| Mineral association | Au | Ag | Cu | S |
|---|-------|-------|------|------|
| Au-Ag phases in pyrite from quartz-chalcopyrite paragenesis | 91,60 | 8,30 | - | - |
| | 90,75 | 9,25 | - | - |
| | 87,35 | 12,65 | - | - |
| Au-Ag phases in bismuthinite-aicinite paragenesis | 67,95 | 27,75 | 1,55 | 0,10 |
| | 67,45 | 27,65 | 0,45 | 0,10 |
| Au-Ag phases in bornite-sphalerite paragenesis | 75,80 | 22,80 | - | - |
| | 73,30 | 25,10 | - | - |
| | 73,20 | 26,10 | - | - |
| | 61,50 | 37,70 | - | - |
| Au-Ag phases in galena-gold paragenesis | 60,56 | 39,44 | - | - |
| | 60,30 | 39,70 | - | - |

described as electrum, was found in the same ore type, especially in the bismuthinite - aicinite parageneses. The paragenesis also includes vitechinite, tetradimite, claustalite, emplectite, hessite and native bismuth forming altogether fine veinlets in the chalcopyrite. The silver content in electrum is about 27 wt.%; minor quantities of Cu (0.4 - 1.5 wt.%) were also registered. The sizes of electrum inclusions are about or over 100 mkm, up to 1 - 2 mm and determine it as a coarsegrained.

The Au-Ag phases in bornite-sphalerite paragenesis from the Zidarovo ore field have a typical zonal texture marked by the increase in Ag content in the peripheral part. Phases with high content of silver associate with galena from the galena - gold paragenesis in the marginal part of the deposit. These regularities in the distribution of Au-Ag phases are in agreement with the common regularities for mineral zonation in the ore field. Au-rich phases associate with high temperature mineral parageneses near the Zidarovo intrusive, while Ag-rich phases tend to the marginal parts, respectively to the end of the ore-forming processes.

Au-Ag phases in the Bacadjic ore field demonstrate similar regularities in general as compared to those described above in the Zidarovo ore field. Part of them associate with the early formed Cu-Au-Bi mineral association where inclusions of native gold could be found together with chalcopyrite, pyrite, bismuthinite, peccoite, chlorite and quartz (Bonev, 1973). The electrum is more typical in association with galena in later basemetal-gold association. The last portion of Au-Ag phases contains minor quantities of Ag and their sizes are larger than 70 mkm.

The Au-Ag phases from the Rossen ore field were found in the Rossen, Stachanov, Meden Rid and Sarnecshco Kladenche deposits. They associate with pyrite, chalcopyrite and carbonates mainly as finegrained inclusions (30 - 40 mkm) and rarely up to 80 - 100 mkm as coarsegrained. The Ag content in them varies from 21 to 34 wt.% (Table 4), so they could be described as electrum. Few findings of native gold containing 10 - 13 wt.% Ag in association with carbonates were reported by Antonova (unpublished data). Its spatial relation with sulfides and carbonates suggest possibilities that gold crystallized as native gold at the beginning of the ore-forming process, later as electrum and, at the final stages, again as native gold.

The lateral distribution of Au-Ag phases in the ore field is characterized by a tendency of significant decreasing in the SE direction. The number of the

Table 4: Chemical composition of Au-Ag phases from the Rossen ore field by electron microprobe analyses (in wt. %)

| Mineral association | | Au | Ag | Cu | Fe |
|---------------------|------------------------------|-------|-------|------|------|
| 1 | Au-Ag phases in chalcopyrite | 72,40 | 27,60 | - | - |
| | | 76,96 | 23,04 | - | - |
| | Au-Ag phases in pyrite | 72,75 | 27,25 | - | - |
| | | 73,21 | 26,79 | - | - |
| 2 | Au-Ag phases in chalcopyrite | 78,18 | 21,82 | - | - |
| | | 77,34 | 22,66 | - | - |
| 3 | Au-Ag phases in chalcopyrite | 71,61 | 26,16 | 1,66 | 0,58 |
| | | 71,60 | 26,16 | 1,65 | 0,57 |
| | | 70,12 | 29,78 | 0,20 | - |
| 4 | Au-Ag phases in chalcopyrite | 70,81 | 29,19 | - | - |
| | | 70,58 | 28,39 | - | 1,03 |
| | | 71,20 | 27,58 | - | 1,22 |
| | | 68,45 | 30,22 | - | 1,33 |
| | | 77,69 | 21,56 | - | 0,75 |
| | | 65,77 | 33,42 | - | 0,81 |
| | | 64,52 | 34,08 | - | 1,39 |

Ore deposits:

- 1 - Rossen
- 2 - Stachanov
- 3 - Meden Rid
- 4 - Sarneshco Kladenche

gold-bearing inclusions is higher in the Rossen and Stachanov deposits, it is very limited in the Sarneshco Kladenche, and none were observed in the Propadnala Voda and Chiplaka deposits (SE part of the ore field). Another significant feature in the spatial distribution of Au-Ag phases in this ore field is the distinguished vertical zonation. Most of the findings were observed in samples from the upper levels (No 75,240,280,400), while they are very rare at lower levels. The maximum appearance of Au-Ag phases was observed at level No 400 in the Rossen and Stachanov deposits (NW part of ore field).

DISCUSSION

The data summarized above show that finegrained Au-Ag phases predominate in all copper deposits from the Srednogorie zone associating preferably with the main stages of sulfide mineralization. Chalcopyrite and pyrite are the most common host minerals in which Au-Ag phases from inclusions sized between 2 and 40 μm . Inclusions sized less than 2 μm have not been established, although some investigations concluded that the larger part of Au-Ag phases in ore deposits is in a finelydispersed form (so called "dust gold"). It should also be mentioned that nowadays studies on Au-Ag phases in ore deposits discredits the previously widely spread idea of the isomorphic presence of gold in the crystal lattice of some minerals, as it was experimentally proved for silicate minerals (Jushko-Zacharova et al., 1986). The most probable form of presence of finelydispersed gold in pyrite, sphalerite and magnetite is as microinclusions on the crystal face of growth or as atomized dispersion in dislocations of the crystal lattice. Minor quantities of gold could be presence in isomorphic

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form in minerals like pyrothine, galena and chalcopyrite (experimental data by Mironov, 1984 in Jushko-Zacharova et al., 1986).

The finegrained Au-Ag phases in copper deposits from the Srednogorie zone fill up commonly fine fractures in chalcopyrite and pyrite or occupy off interstitial spaces between mineral grains. Their texture is xenomorphic, very often elongated and no single crystals are observed. These peculiarities suggest that the finegrained Au-Ag phases were formed later than the crystallization of the main sulfide minerals. Their micronic sizes are due to the minor quantities of gold and silver in the hydrothermal fluids as it is typical of all precious metals in such types of deposits. Based on the studies mentioned above (Mironov, 1989) it could be assumed that part of the gold and the silver has isomorphic presence in the crystal lattice of chalcopyrite. This quantity is not "lost" from an economic point of view, because isomorphic gold and silver could be extracted during the metallurgical processing of copper concentrate. The more serious problem for practice is the probable presence of Au-Ag microinclusions in pyrite. Their behavior during the technological operations needs further detailed study for more successful final extraction.

The coarsegrained Au-Ag phases have a larger distribution at the end of the main copper mineralization and they partly associate with later Pb-Zn parageneses in the massive sulfide and vein deposits from the region. Their rare presence in the porphyry-copper deposits could be explained by taking into account the specific genetical conditions of the ore-forming process in these deposits. Due to the deeper levels in which these processes take place, it could be assumed that the ore-forming system should be relatively closed in comparison to that in the massive sulfide and vein deposits. The open spaces are very limited and no favorable conditions for crystallization of well-shaped individuals or bigger aggregates exist. The system is relatively closed to the end of the ore-formation and the processes of mineral recrystallization and recombination of the elements are also very limited or do not exist at all. The greater amount of elements in the hydrothermal fluids form their own minerals during the main copper-sulfide stage of mineralization. The final fluids transport a very small quantities of elements and the gold and the silver probably are not enough to form their own phases. The restricted volume and the low chemical activity of the final fluids do not stimulate the extraction of silver and gold from the early formed ores and their re-accumulation in the Pb-Zn veins from the marginal parts of the porphyry-copper deposits.

The data established for the vein copper and massive sulfide ores show that they are formed in more open systems, not so deeply disposed. The volume of the open spaces in which the processes take place, is larger and the more dynamic changes in the physical and chemical conditions are suitable for the formation of bigger mineral aggregates, even well-shaped single crystals. As it was mentioned above, evidence for recrystallization and additional formation of Au-Ag phases sized from 70 μm up to several mm could also be found in some deposits from these types. These phases are localized as usually in the periphery parts of the deposits along with the latest mineral associations.

The chemical composition of the Au-Ag phases is characterized by a predominance of silver rich phases (electrum) in the porphyry-copper and vein deposits and a larger distribution of phases containing less than 20 wt.% Ag in the massive sulfide deposits. The problem of stability for Au-Ag compositions is still an object of a discussion, but the opinion that there are several intervals with different degree of stability in this system is supported more actively (Jushko-Zacharova et al., 1986). The range of silver

content 20 - 22 wt.% was established as the most stable, as well as, the instability of the solid solution increases and certain phenomena of destruction could be observed above this range. Two different ranges in the Au-Ag system could be determined from the samples studied. The first one includes the compositions (2-13 wt.% Ag) of native gold and the second one (20-30 wt.% Ag) is typical of the electrum composition.

The predominant number of the Au-Ag phases from porphyry-copper and vein deposits occupy the range 20 - 30 wt.% of silver content and only a few analyses from the latest Au-Ag phases in the Zidarovo ore field are close to 40 wt.% Ag content.

The irregular dispergation is typical of the samples studied, but silver-rich boundaries were established in some grains. This could be the result of autodiffusional processes which increase the stability of the phases previously formed. The silver differentiation is more distinctly expressed in the massive sulfide deposits, but it can be found in the vein deposits formed at higher levels (such as the Zidarovo ore field) or even in upper parts of the porphyry-copper deposits (Medet). The temperature of the ore-forming process has a very important influence on the deposition of Au-Ag phases. Comparing their features in the different deposits, it should be noted that low temperatures of ore-formation (200-250°C) in the massive sulfide deposits predetermine relatively low-silver phases (finegrained and coarsegrained), as well as, the higher temperatures (300-450°C) in the porphyry-copper deposits stimulate the deposition of finegrained silver-rich phases. The vein copper deposits have an intermediate temperature position (350-250) and the Au-Ag phases show features characteristic of the other two types. The lower temperature conditions are also suitable for mineral formation in which the gold takes part in different composition with elements like tellurium (kostovite, sylvanite) ore with tellurium and plumbum (nagiagite) established in the massive sulfide ores in the Chelopech ore field.

Copper and iron are found as trace-elements in some of the phases studied. Their content varies in the range of 1 - 2 wt.% and only in a sample from the Chelopech ore deposit, the content of copper increases up to 16.02 wt.% which characterizes it as "copperferrous" gold. These two elements are among the usual compounds in the Au-Ag phases from sulfide deposits, although diffusional influence from the chalcopyrite matrix could be accepted in cases when grains with minor sizes were analyzed (e.g. the samples from the Elatzite ore deposit). Minor quantities of thallium (0.13 - 0.35 wt.%) are registered in coarsegrained gold from Chelopech, which is an element reported for the first time as a trace-element in Au-Ag phases.

The data obtained confirm that the formation of Au-Ag phases in the massive sulfide and vein copper deposits take longer time and they are more varied in their morphological features and chemical composition in comparison to these in the porphyry-copper deposits from the Srednogorie zone.

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