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STUDY OF SOME QUESTIONS OF GOLD-BEARING OF THE ORE VEINS OF KREMNICA BY THE METHOD OF ELECTRON MICROSCOPY

(Figs. 1—11)

Abstract: In this paper the results of study of electrum from the subvolcanic deposit of Kremnica by the methods of electron microscopy are presented. Forms of occurrence of invisible electrum in vein quartz and the morphology of visible electrum are described. The results of electron microscopy are confronted with the results of paragenetic study of ore veins.

Geology of the Ore Field and Ore Veins

Kremnica, the deposit of gold, silver and antimonite, is situated in an area formed by Miocene volcanites appearing in extensive areas in the Mountains of Kremnica and Banská Štiavnica in Central Slovakia. The neovolcanites of Central Slovakia are a part of subsequent volcanism of the Carpathian orogene and their position is tectonically bound to the crossing of a young lineament of N—S direction with Carpathian structures of NE direction. The essential portion of the volcanism of the Mountains of Kremnica was taking place in the Upper Tortonian and Sarmatian. The volcanic rocks are represented by the following types in the scheme of succession: pyroxenic andesites that are completely predominating, pyroxene-amphibolic andesites, amphibole-biotitic andesites, rhyolites. The final volcanism of Pliocene age is represented by basalts.

The ore bearing hydrotherms are bound to an advanced stage of differentiation of the magma focus and were ascending as late as after the rhyolite period, to the end of the Sarmatian possibly reaching up to the Pliocene.

The volcanic complex in the centre of the mountain range rests on Mesozoic dolomites.

The present day thickness of the volcanites, in which gold-bearing veins are exploited in Kremnica, exceeds 1000 m. The deposit is formed by about 120 veins, which are gathered into two vein systems: Ist vein system: (Schrämmen Vein, Main Vein). IInd vein system (Gold Vein, Krížna Veins Ore Veins, Helena Vein). The Ist vein system is characterized by considerable thickness of the ore veins commonly reaching about 10 m and up to 70 m in some sections and the electrum is present in the invisible form only. The IInd vein system is characterized by veins of small to medium thickness and besides the electrum invisible macroscopically in the ore veins bonanzas formed by rich concentrations of visible electrum occur. The principal vein structures are of NNE direction, parallel to regional fault structures.

The pyroxenic andesites within the ore field are affected by mass propylitization and alterations around the joints that form a zonal structure. The most external zone is that

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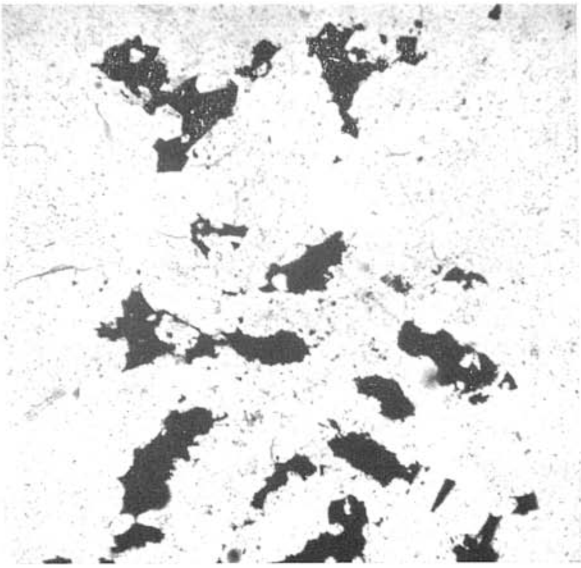

Fig. 1. Electrum (dark-coloured), xenomorphic compared to vein quartz, bound to small joints of tectonic origin. Kremnica, Ferdinand Pit, Gold Vein, thin section, magnif. 65 ×, parallel nicols. Photo by L. Osvald.

of chloritization, then those of adularization, mica clay, and kaolinite and the zone of silification adjoining the ore vein follow.

The process of ore mineralization was accompanied by tectonic unrest manifesting by repeated crushing of the vein filling so that on the basis of six pulses of tectonics of interminaralization periods of supply could have been distinguished and geochemical development of the hydrothermal process studied.

The position of the gold-silver formation of Kremnica within the range of ore formations of the neovolcanites of Central Slovakia is described more in detail in the work by M. Böhmer, J. Štahl (1968).

Paragenesis of Ore Veins and Position of Their Electrum

The six periods of supply that could have been found out by the study of macrostructures of the ore filling may be divided into two stages of development separated by a relatively strong tectonic phase and also showing considerable differences in paragenesis. The older stage of development of formation of gold-silver veins and the younger one of antimonite were distinguished. We apply the conception of the supply period and development stage in the sense of J. Kutina (1963).

The development stage of gold-silver, the subject of our study by the methods of electron microscopy, is characterized by periods of supply nearly exclusively formed by hydrothermal quartz. The content of gold attains about 3.7 g/t in richer parts of the ore veins, the other parts of the veins have the contents of gold about 2 g/t only. The contents of Ag are most frequently 3—7 times higher. Gold has a high content of silver in the form of electrum. Beside that silver is also present in several own minerals. The ore minerals appear in the vein quartz in very small amounts only. The most frequent of them is pyrite, attaining only 3 % in the vein filling. The other ore minerals — sulphides of coloured metals, sulphides and sulpho-salts of Ag are only accessory in vein quartz. In the stage of development of antimonite the essential part of the ore filling is formed by dolomitic calcite, metacolloidal quartz and chalcedony. From ore minerals considerable amounts of markasite and antimonite are present. In some younger vein structures antimonite attains minable concentrations with contents of about 3 % Sb. The supply of Au lowered considerably in this period, in spite of that its contents attain about 0.4 g/t and those of Ag about 1 g/t in antimonite ore. In sections of veins without antimonite mineralization the contents of Au, Ag are even lower and therefore young vein structures with this type of mineralization had been since long ago considered as unimportant from the stand-point of exploitation of gold and silver.

The temperatures of crystallization of quartz of the development stage of gold-silver measured by the method of homogenization of gaseous-fluid inclusions and of decrepitation show average values of 270—290 °C. The development stage of antimonite showed temperatures of hydrothermal solutions essentially lower concluding assording to the paragenesis.

The occurrence of electrum in ore veins has its characteristic features that were found out by minerographic methods of investigation. The principal part of electrum in the ore veins is present to the end of the development stage of gold-silver. In the Ist vein system with only invisible electrum present are its richer concentrations found to the end of the period of supply indicated by accumulations of pyrite, in which electrum is accompanied by the typical varied association of minerals: adular, baritecoelestine, chalcedony, arsenopyrite, goethite, sphalerite, chalcopyrite, galenite, proustite, polybasite, pyrargirite. Electrum of this association is present partly as submicroscopic, partly within the reach of visibility under the optical microscope. We suppose electrum in this association to be present in invisible form because it is scattered in larger amounts of pyrite.

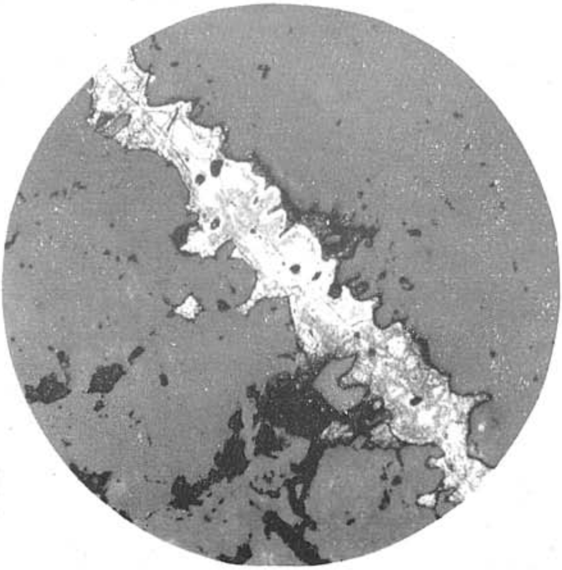

Fig. 2. Vein of electrum (light-coloured) in quartz vein (dark-coloured) with irregular zonal texture conditioned by various ratio of Au, Ag. The zones richer in Ag are grey. Kremnica, Ferdinand Pit, Gold Vein, polished section, magnif. 190 ×. Electrum etched with vapour of aqua regia. Photo by L. O s v a l d.

Analogous situation in the occurrence of electrum is in the IInd vein system, where considerable amounts of electrum are also concentrated to the end of the development stage of Au-Ag. Rich concentrations of electrum, however appear there in the form of bonanzas of electrum visible macroscopically. We explain this difference in contrast to the Ist vein system by essentially lower contents of pyrite in the vein filling. Also in this case the electrum is accompanied by varied association formed by the minerals: hematite, tetrahedrite, bournonite, polybasite, proustite, pyrargirite, molybdenite. The rich ore forms about 15—20 % of exploitation and for its high content of Au and Ag it is of great practical importance.

The study of electrum visible macroscopically as well as of that visible under microscope proved its predominating part to be of epigenetic character in contrast to older generations of quartz and pyrite, as it is typical of the most hydrothermal deposits of gold. Precipitation of electrum from hydrothermal solution is nearest in time to precipitation of varied associations of minerals, we have mentioned for both the vein

Fig. 3. Finely dispersed porphyry electrum, mostly concentrated in zones of inhomogeneity of grey vein quartz from the Helena Vein. Two-degrees replica of natural fracture surface, magnif. 9250 ×. Photo by M. H a r m a n.

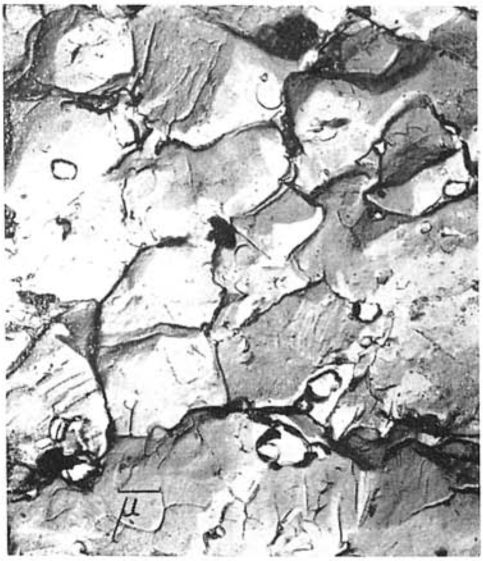

Fig. 4. Finely dispersed porphyry electrum, mostly concentrated in zones of inhomogeneity of grey vein quartz from the Helena Vein. Two-degrees replica of natural fracture surface, magnif. 5750 ×. Photo by M. H a r m a n.

systems and which are a reliable mineralogical indicator of the richer sections of ore veins. A typical example of the occurrence of electrum in vein quartz is shown in fig. 1.

Another characteric feature of the ore veins of Kremnica are widespread colloform structures and textures or their relict found in vein quartz, pyrite, marcasite, antimonite and visible electrum. The structure of electrum was examinated in mineragraphical studies by aid of structural etching by vapour of aqua regia. At visible electrum its inhomogeneity formed by zones with different ratio of Au-Ag was found out by this method, interpreted on the basis of the morphology of the zones as rhytmical coagulation of gel of Au-Ag with variable ratio of both the constituents. An example of epigenic vein of electrum in vein quartz etched by vapour of aqua regia with typical structure is shown in fig. 2. More detailed data about the paragenesis of gold-bearing veins of Kremnica are treated in the works by M. B ö h m e r (1964, 1965).

In spite of detailed minerographic study some important questions remained unsolved, for solution of which electron microscopy is suitable. We therefore were aimed at the study of these two problems mainly:

1. Form and character of occurrence of submicroscopic electrum in vein quartz that forms the part completely prevailing in the vein fillings of Kremnica.

2. Ultramicrotexture of the surface of gold particles of electrum visible macroscopically, on the basis of mineragraphic study of which the supposition of rich concentrations conditioned by coagulation of Au, Ag was expressed.

Methods of Work

For the study under electron microscope the method of two-degrees replicas of natural fracture surface was employed. In the case of less diverse surfaces we employed acetylbutylcellulose foil of Czechoslovak production, soluble in chloroform or the foil „Triafol" or the blue Japanese foil at some relatively smooth surfaces of gold covers for making the first-degree imprint. Preparation was usually carried out at least by two kinds of foils in order to annul the possibility of the presence of artefacts caused by occasional different replicational qualities of the individual foils. It is to remark that in confrontation of the results in essentials no differences concerning the morphology have been found out, slight differences were only evident in the degree of distinguishing capacity of the individual media. At highly diverse fracture surface we used polystyrene as replication mass.

After shadowing of the first-degree imprint (usually with the alloy of Pt-Pd under an angle of 35°) and carrying a layer of carbon on it membranes carried on supporting nets and used for study by microscope were obtained after dissolution of replication medium in corresponding dissolvent.

Discussion of Results

In literature available we find several brief references about application of electron microscopy in the study of gold. Demonstrations of possibilities of figuring of fine porphyry gold in ore minerals are mentioned in the work by G. S. G r i c a e n k o and K. S. F r o l o v a (1963) who have found gold in the form of elongated swollen particles of the size up to 2 μ in crystals of pyrite and arsenopyrite. These authors, however are not dealing with further evaluation of this observation. The genetic aspects of this finding are evaluated by A. V e l č e v (1965) who tried to trace dependence of the forms of finely dispersed gold in pyrites on the conditions of its origin at the locality of Govežda (Bulgaria) and compared them with the results of J. B u ž o r (1950) and J. V. M a s l e n i c k i (1948) obtained by aid of optical microscope. Interesting crystallographical observations were made by M. G i l l e t (1960) by the method of electron microscopy on finely dispersed gold prepared artificially. Dislocations in very thin lamellar crystals of colloidal fold prepared artificially were treated by R. H. M o r r i s, R. G. P e a c o c k and W. O. M i l l i g a n (1965) by aid of Moirée's patterns under electron microscope.

Regarding to the type of the deposit and the results of analyses of mineralogical samples as well as of working analyses we suppose electrum to be concerned also for particles observed under electron microscope. On the basis of the study of samples from Kremnica under electron microscope we distinguished three modifications of electrum, different in morphology, grain size, crystallographical delimitation and as we suppose also in the circumstances of origin.

They are: electrum of spherical or irregular forms, without any observable crystallographical delimitation, also cubic or octahedral and blade-shaped electrum, already belonging to the category of concentrations visible macroscopically .

In the first phase of our work samples of grey gold-bearing quartz with the same porphyry ores of older periods of supply were studied, being the main bearer of submicroscopic electrum. In this quartz particles of electrum can be observed under optical microscope sporadically only. The studied samples come from the Krížna and Helena veins (IInd vein system) and form the essential mass of exploited ore. Under electron

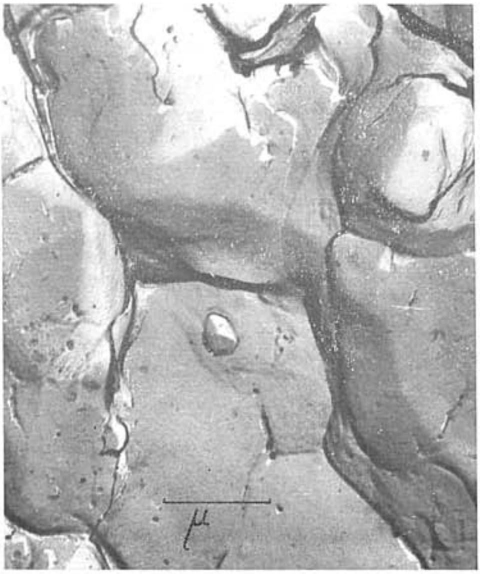

Fig. 5. Porphyry electrum with indications of complete or partial crystallographic delimitation from light-coloured vein quartz of the Krížna Vein — 5th horizon. Two-degrees replica of natural fracture surface, magnif. 14 200 ×. Photo by M. Harman.

Fig. 6. Porphyry electrum with indications of complete or partial crystallographic delimitation from light-coloured, finegrained vein quartz of the Krížna Vein — 2nd horizon. Two-degrees replica of natural fracture surface, magnif. 8830 ×. Photo by M. Harman.

microscope inequigranular ultramicrotexture may be observed here, the individuals of quartz usually forming particles of the size of 2—10 μ, usually with rounded faces without any crystallographical delimitation but sometimes with parallel furrowing of some individuals. Electrum is present here in the form of finely dispersed porphyry ores of the size up to 0.5 μ in spherical or irregular forms, usually sporadical or rarely in clusters. In the most cases the particles of electrum follow zones inhomogeneity of the vein quartz, as small fissures or intergranular spaces between the individual quartz grains. The character of this occurrence corresponds well to the described forms of occurrence of finely dispersed electrum also in other minerals (pyrites, arsenopyrites etc.). The occurrence of electrum in small fissures and intergranular spaces or in the proximity of them as well as the morphology of its particles — elongated shape permit to suppose its younger age in relation to quartz which is older than the producing periods of supply of electrum.

It is only at a small part of electrum grains that the epigenetic character is not quite distinct (fig. 3, 4).

In the quartz veinstuff, already belonging to younger parts of the stage of development of Au-Ag, in which no larger amount of finely dispersed porphyry ore that would influence its colouring (as e. g. the samples of light-coloured vein quartz from the 5th horizon) is present, a rather small amount of porphyry electrum in the form of smaller and larger particles with indication of complete or partial crystallographical delimitation occurs, usually of cubic forms or with combination of cube (001) and octahedron (111). These particles are also different from the preceding ones in their

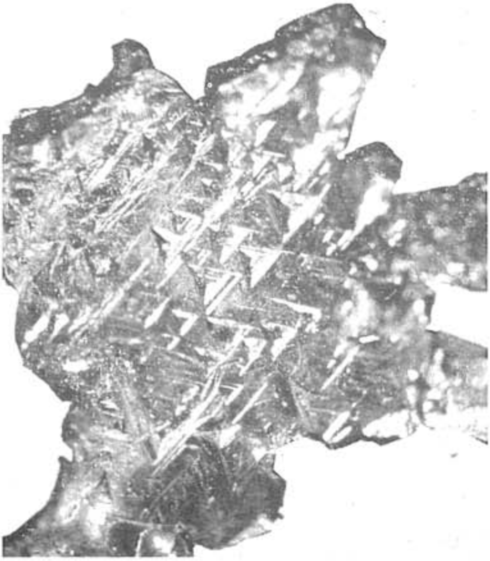

Fig. 7. Zonal pyramides of the surface of gold cover from drusy cavities of the Overlying Helena Vein — 5th horizon. Magnif. 40 ×. Photo by L. Osvald.

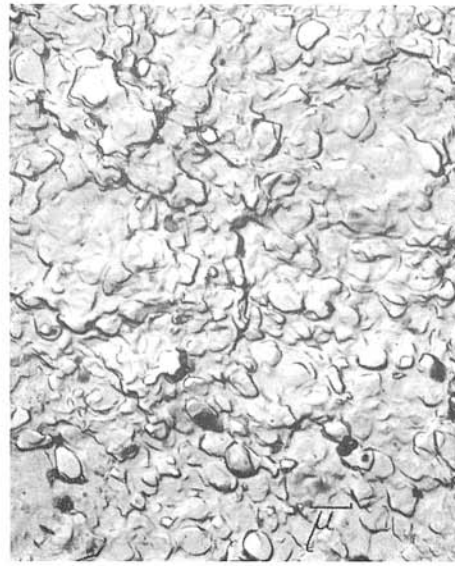

Fig. 8. Globular forms of the surface of the central part of gold cover of drusy cavities from the Overlying Helena Vein — 5th horizon. Two-degrees replica of natural surface, magnif. 5750 ×. Photo by M. Harman.

size, their dimensions usually vary in the limits of 1—5 μ, sometimes also more. In the attached electronograms we see this modification in two different types of the veinstuff. The coarse-grained type of quartz veinstuff (the size of individuals of quartz is up to 10 μ) contains smaller particles of electron of good crystallographical delimitation (fig. 5) while the relatively very fine-grained type of quartz veinstuff (Krížna Vein, 2nd horizon) contains well developed individuals of electrum, sometimes attaining the size observable under optical microscope, in polished sections (fig. 6). In its time of crystallization this type of quartz is near to the main supply of Au-Ag to the end of the development stage and therefore the epigenetic character of electrum is disappearing compared to vein quartz. On the contrary, electrum may be somewhat older than the environment in which it occurs. The question so far remains unsolved if there is any relation between the size of individuals of vein quartz and the degree of crystallographic delimitation of electrum. The possibility of existence of this regularity would be suitable to follow to a larger extent than it is possible under present state of study.

Textural features on the surface of faces of the cubic gold cover in the form of hemispherical round projections are interesting in morphology. Similar features in typical development were found on the faces of large gold covers from drusy cavities.

Large blade-shaped gold covers from bonanzas of visible electrum from drusy cavities of the Overlying Helena vein, 5th horizon, which attained dimensions as large as 3 × 5 mm, display 2 categories of textural features on the surface. They are in first order the known zonal pyramids, visible under optical microscope, with typical transverse furrowing (fig. 7). The picture of the superficial face is largely different

Fig. 9. Two generations of globular forms on the surface of the central part of the gold cover from drusy cavities of the Overlying Helena Vein — 5th horizon. Two-degrees replica of natural surface, magnif. 5750 ×. Photo by M. H a r m a n.

Fig. 10. Porous ultramicrostructure with motives of isosceles triangles from peripheral parts of the gold cover from drusy cavities of the Overlying Helena Vein — 5th horizon. Two-degrees replica of natural surface, magnif. 9250 ×. Photo by M. H a r m a n.

under electron microscope. Hemispherical protuberances several tenths of μ wide with sharply limited margins may be observed in it. In individual cases these protuberances are also of elongated shape (fig. 8 and 9). The size of these forms is 1—2 μ in central parts of the gold covers, in peripheral parts it diminishes and passes into porous to spongy ultramicrostructure with slightly distinct transverse furrowing in three directions, forming a pattern with the motive of isosceles triangles representing, as we suppose, the fundamental elements of crystallographic delimitation (fig. 10). A detail of the surface of one protuberance taken under large magnification showed further particularities of the ultramicrostructure in the form of undeep flat irregular depressions of various shape (fig. 11). In one sample (fig. 9) 2 generations of these forms could have been identified, more rounded and larger ones with less sharp delimitation, and younger smaller, sharply limited, with more distinct relief, partly growing on the former. This type of electrum showed typical colloform structures with zones of different portion of Au and Ag in mineragraphic study. As we did not have the possibility of studying qualitative differences of this ultramicrotexture, it may be supposed only that the individual morphological forms represent colloform formations with variable representation of Au and Ag.

Conclusions

The study of electrum from the ore veins of subvolcanic type of Kremnica by the method of electron microscopy followed detailed paragenetic investigation, in the course of which maximum supply of Au-Ag was found out to have taken place to the end of the development stage of Au-Ag formed by several periods of supply of hydrothermal quartz. The younger stage of development is characterized by Sb mineralization. Typical association of electrum formed by varied paragenesis of nonmetallic minerals, common sulphides and sulpho-salts of Ag was found. In veins of small thickness electrum is present in the form of bonanzas of visible electrum, in which zonal structure with different portion of Au-Ag in the individual zones was proved by etching with vapour of aqua regia. The morphology and order of these zones permits to suppose that coagulation of colloids of Au-Ag (electrum) from hydrothermal solution was taking place.

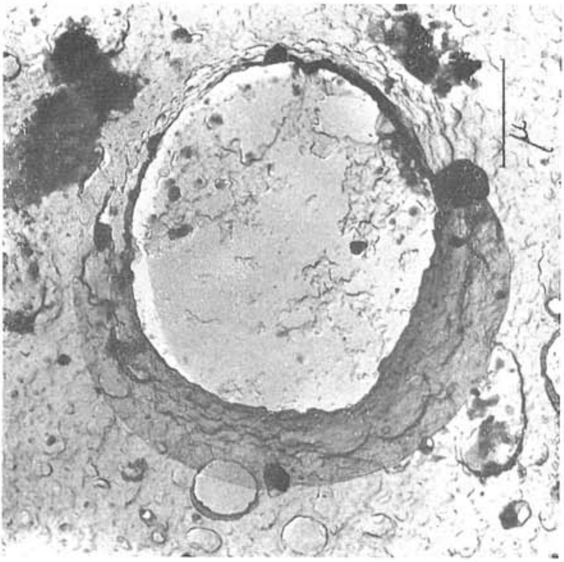

Fig. 11. Detail of ultramicrostructure of globular excrescence from the central part of the gold cover from drusy cavities of the Overlying Helena Vein — 5th horizon. Two-degrees replica of natural surface, magnif. 14 200 ×. Photo by M. Harman.

The methods of electron microscopy were employed to trace various forms of occurrence of electrum, wherein the following modifications of it could have been distinguished:

1. Electrum in older periods of supply of hydrothermal quartz attains the size of 0,5 μ in the form of spherical, elongated or irregular shapes. The majority of it is bound to zones of inhomogeneity of the vein quartz and its supply may be parallelized with the period of main supply of Au-Ag to the end of the stage of development of Au-Ag.

2. Electrum of young generation of vein quartz, which is near to the end of the stage of development of Au-Ag, attains dimensions from 0,3 to 4 μ and is characterized by regular crystallographic delimitation. This electrum crystallized at the same time with the vein quartz.

3. At last the study of the surface of gold covers from bonanzas of electrum visible macroscopically shows mainly typical spherical or globular ultramicrostructure that we elucidate by coagulation of gels of Au-Ag comparing with the results of mineragraphic study.

As it is evident from our study, the combination of optical, mineragraphic investigation and electron microscopy in the study of gold deposits provides for results which are a suitable supplement in the sphere of the study of gold visible macroscopically as well as in the form of insignificant scattered gold. This information may be used, as we suppose, not only for solution of genetic and morphological problems but also in the branch of technology and dressing of gold-bearing ores.

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