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MINERALOGICAL CHARACTERISTICS OF SUPERGENIC MINERALIZATIONS IN COPPER DEPOSITS OF CENTRAL SREDNOGORIE

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ABSTRACT

82 minerals and their varieties have been established in the composition of the supergenic mineralizations in copper deposits of Central Srednogorie , i.e. 30% of all described for the region, 12 of them being new for our country .The following characteristic supergenic minerals have been found from the comparative mineralogical analysis : hematite, hydrohematite, goethite, lepidocrocite, malachite, azurite, kaolinite, montmorillomite, bornite, chalcococite, covellite, djurleite, digenite, gold. Specifical minerals for copper and pyrite deposits are : melanterite, gypsum, chalcodone, opal, chalotrichite, alum , sulphure, amilite; for copper and porphyritic: hydromica, hydrogoethite, elite, diskite, halloysite, nacrite, maghemite, martite, mushketovite, chrysocolla, chalcanthite, brochantite, thenardite, tenorite, cuprite, copper, antlerite and for copper molybdenum and porphyritic: specularite, hematolite, hydro-goethite, molybdite, chrysocolla, spherosiderite. Supergenic minerals have a different qualitative disribution. Special mineralogical characteristics are a reliable criterion for exploring new copper deposits in the region and for determining the character of hypogenic mineralization. Supergenic mineralizations of copper deposits are a source for production of copper, gold, kaolinite and other mineral reserves.

INTRODUCTION

Mineralogy of supergenic mineralizations is various. Over 25% of all discovered mineral types and varieties have been found in them. 82 minerals and their varieties or 30% of the established up to now in this region have been described in the composition of supergenic mineralizations of copper deposits in Central Srednogorie. 14 of them are completely new for our country. Author has carried long-lived mineralogical investigations of supergenesis of copper and pyrite deposits of Radka, Elshitza, Krassen and Chelopech, of copper and porphyritic deposits of Tzar Assen, Assarel, Vlaikov vruh, Petelevo and Popovo dere and of copper and molybdenum and porphyritic – Elatzite and Medet. Results of these studies are being generalized and added in the present paper. The main target is to establish the characteristics of supergenic mineralizations for three types of genetic deposits by comparable mineralogical analysis. This helps in drawing mineralogical criteria when making an assessment deposits. The zones of supergenesis are a source of mineral raw materials. Studing their mineral composition helps in improving their production and treatment technology.

METHODICS

Terrain observations have been made for a long time not only of ground surface exposures but of the entire depth of the zones of oxydation and of secondary sulphide processing during the entire period of ore production from copper deposits in the regoin. The selected over 2 500 pieces of samples have been observed under a bineye-lense stereomicroscope. These are mineral mixtures forming porous cavernous and spongy aggregates. 320 thin sections have been studied in a suitable and reflected light. Optical properties such as: reflection, bi-reflection, colour, effect of anisotropy, internal reflections, diagnostic fretting and reactions of colouring have been applied. Many of the optical inverstigations have been carried out in cooperation with E. Afanasieva and M. Isaenko and have been compared to the published by them in 1981 determining tables.

Over 160 powderd samples have undergone a semi-quantitative spectral analysis, quantitative chemical analysis of Cu, Au, Ag, Pb, Zn, Fe, Mo and complete silicate analysis. 198 monomineral samples have been studied under bineye- lense stereomicroscope. Powder radiogrammes (96) and radiodi-fractogrammes (56); investigations with intra-red spectroscopia (65); differential and thermal analysis (28) have been made in the laboratories of UMG. 356 electronic and microscopic investigations have been made in MGRI – Moscow by enlargement from 2000 to 8000 times and microdifraction of separate mineral particles. 95 minerals have been studied by microdrilling analysis in Evrotest – Ltd - Sofia and in IGEM-Moscow. Each of the mentioned methods has a different permissing ability. Mineral diagnostics has been done by several methods. Quantitative distribution of supergenic minerals has been studied.

Table 1 shows the quantitative distribution of supergenic mineralizations of the main genetic types of copper deposits in Central Srednogorie in a reductional and oxydational stage. It generalizes the earlier made studies of the author published in 8 publications given in Referances.

RESULTS

Mineralogical characteristics of supergenic mineralizations of copper and pyrite deposits

During the reductional stage of mineral formation in the zones of secondary sulphide processing of copper and pyrite genetic type of deposit considerable quantities of chalcocite, bornite, covellite, anilite and of the non- ore minerals- kaolinite and montmorillonite have been formed. Secondary typical minerals are gold, djurleite, digenite, neodigenite and from the nonore minerals- chalcedone, halloysite and hydromica. Rarely met minerals are elite and hydrobiotite. Hydrogenic minerals are formed in a wide space from waekly acidic to neutral medium according to the scheme of E. Afanasieva and M. Isaenko (1981) using the data of R. Garelse and V. Schebrina. The quantitative storage of copper sulphides determines the industrial signifficance of the zones of secondary sulphide processing for copper, gold and silver production. Typical hypergenic minerals are anilite, neodigenite and bornite. (Table 1).

Cousiderable quantities of hematite, goethite with ferrous oxides and hydroxides in the mineral mixture "limonite", chalcedone, alum, melanterite, yarozite are beeing precipitated in the composition of oxidizing zones of copper and pyrite deposits (fig. 1). Kaolinite, hydromica, montmorillonite, gypsum, chalcanthite, malachite, azurite, lepidocrocite, hydrohematite, elite, diskite, halloysite, halotrichite, sulphure, cuprite are of secondary quantitative deposition. Tenorite, opal and chrysocolla are rarely met. Gold is a typical metal. Gold content in the zones of oxidation of copper and pyrite deposits varies from 1g/t (Radka deposit), 2g/t (Chelopech and Krassen deposits) and 3g/t (Elshitza deposit). That defines the zones of oxidation as a source of gold production (fig. 4).

Mineral formation is realized in an acidic medium as a result of which considerable quantities of sulphate minerals are being deposited. That is a characteristic feature of the zones of oxidation of copper and pyrite type deposits. The deposition of considerable quantities of hematite and "lemonite is typical due to which local population has been using them for ochre since ancient times.

Mineralogical characteristics of supergenic mineralizations of copper and porphyritic deposits and copper and molybdenum and porphyritic deposits

Considerable quantities of chalcocite, covellite, djurleite and digenite are being deposited during the reductional stage of these genetic type deposits. Secondary minerals are martite and specularite. Quantitative deposition of kaolinite, diskite, hydromica, halloysite and montmorillonite is typical for copper and porphyritic deposits. Gold can be rarely found. Copper contents in the zones of secondary sulphide processing vary from 0,2 to 3,5%; gold- from 0,06 to 1g/t; silver- from 5 to 20g/t; molybdenum- from 1 to 10g/t; tellurium- from 0,5 to 20g/t; bismuth- from traces to 0,9g/t. That determines their importance for copper, gold and silver production and from copper-porphyritic type deposits (Assarel) for kaoline mineral raw material as well.

Mineral formation took place in weakly acidic to acidic raw material. Specific minerals for copper and porphyritic deposits are: maghemite, martite, mushketovite, and for copper and molybdenum and porphyritic deposits- specularite.

Considerable quantities of montmorillonite, kaolinite, halloysite (fig. 2) goethite,lepidocrocite and ferrous oxides and hydroxides in the mineral mixture "limonite", cuprite, malachite, azurite, chalcodone, chalcanthite, chrysocolla, brochantite are being deposited in the zones of oxidation of copper and porphyritic deposits. Copper, hematite, tenorite, hydrogoethite, elite, diskite, alunite and alum have secondary quantitative deposition. Typical for these zones minerals are rarely found: nacrite, antlerite, spangolite, thenardite, dioptase and electrum. (Table 1). Mineral content of the zones of oxidation of copper and molybdenum and porphyritic deposits is characteristic for the smaller quantitative deposition of clay minerals (Table 1). Typical supergenic minerals in their composition are: specularite, hematolite, molibdite, (fig. 3), chrysocolla, malachite, azurite, spherosiderite and hydrogoethite. The following minerals can be rarely met: kottigite, libethenite, mimetite, atelestite, chalcophyllite, feromolybdite, goslarite, alunogen, rosenite,linarite,szomolnokite, anglesite, montmozillonite. The only malachite with juwelleric qualities in their content has been found.

Table 1. Quantitative distribution of supergenic minerals in reductional and oxidational stage of genetic type deposits

Class Mineral	Reduc Cu pyrite	tion Cu porphyrite	stage Cu-Mo-porphyrite	Oxida Cu pyrite	tion Cu porphyrite	stage Cu-Mo-porphyrite
1	2	3	4	5	6	7
Elements						
Gold	+++	++	++	+++	+++	++
Copper					++++	++
(Electrum)					++	
Sulphuze				+++	+	+
Sulphides and sim. compounds						
Bornite	++++	+++	+++	++	++	++
Chalcocite	+++++	+++++	++++	++	++	++
Anilite	++++					
Djurleite	+++	++++	+++			
Digenite	+++	++++	+++			
Covellite	++++	+++++	++++			
Wittichenite		++				
Aikinate		++				
Neodigenite	+++					
Oxides and hydroxides						

1	2	3	4	5	6	7
(Maghemite)		++++			++	++
(Martite)		++++	+++		+++	+++
(Mushketovite)		+++				
(Specularite)		++++	++++		++	+++
Hematite				+++++	++++	+++
Hydrohematite				+++	+++	+++
Goethite				+++++	+++++	++++
Chalcotrichite					++	
Hydrogoethite					++++	+++
Lepidocrocite				+++	++++	+++
Srelimonite				+++++	+++++	++++
Tenorite				++	+++	++
Cuprite				+++	++++	++
Fe wad						+
Zincite						+
Claudetite						+
Fluellite						+
Silicates						
Kaolinite	++++	+++++	+++	++++	+++++	+++
(Illite	++	+++		+++	++++	+++
Diskite		+++++		+++	++++	++
Nacrite					++	
Halloysite	+++	+++	++	+++	++++	+++
(Ferrihalloysite)					++	
(Metahalloysite)					++	
Hydromuscovite					++	++

1	2	3	4	5	6	7
Hydromica	+++	+++++	+++	++++	+++++	++++
Ewladonite					++	
Montmorillonite	++++	+++++	++	++++	+++++	+++
Chrysocolla				++	+++	++
Hydrobiotite	++	++	++	+++	+++	++
Dioptase					++	
Edingtonite						
Phosphates, arsenates, vanadates						
Scorodite					+	
Andrusit					+	
Hemalolite					+	++
Kiottilite						+
Libethenite						+
Mimetite						+
Atelestite						+
Chalcophyllite						+
Wolframs and molybdates						
Molybdite						++
Feromolybdite						+
Sulphates						
Alunite				+++	++++	++
Alum				+++++	++++	+++
Barite					++	
Melanterite				+++++	+++	++
Jazorite				++++	+++	++
Gypsum				++++	+++	++
Chalcanthite				++++	+++++	+++
Brochantite					+++++	++
Halotrichite				+++	++	++
Thenardite					++	++
Goslarite						++

1	2	3	4	5	6	7
Antlerite					++	
Spangolite					++	
Alunogen						++
Rosenite					++	++
Linarite						+
Szomolnokite						++
Anglesite						++
Montmorillonite						+
<u>Carbonates</u>						
Calcite					++	
(Mn calcite)					++	
Azurite				++++	+++++	++++
Malachite				++++	+++++	++++
Juveliren malachite						++
Spherosiderite					++	++

Note: mineral is: +++++ in considerable quantities
++++ in secondary quantitative deposition but deposition
+++ in small quantities
++ rarely found
+ very rarely found

Cu-copper; Cu- Mo- copper- molybdenum ;sulphides and simular compounds.

Mineral formation took place in acidic and slightly acid medium for copper- porphyritic type depositsand in neutral medium for copper- molybdenum porphyritic type deposits.

CONCLUSION

Industrial minerals for secundary sulphide processing zones for all copper deposits of Central Srednogorie are: chalcocite, covellite, djurleite, digenite, bornite, gold. Industrial minerals for oxidation zones are: gold, alum, hematite- for copper-pyrite deposits, malachite, azurite, molybdite- for copper- molybdenum- porphyritic type deposits. Gold (fig. 4) in greatest quantities is in the content of oxidation zones of copper- pyrite deposits. Pouring on the aggregates with acid brings to gold particles with the dimension of 1 mm (fig. 5).

Figure 1. Zone of oxidation of copper and pyrite deposits: hematite, goethite, yarosite and ferrous oxides replace compact pyrite, plished section, increased 410x.

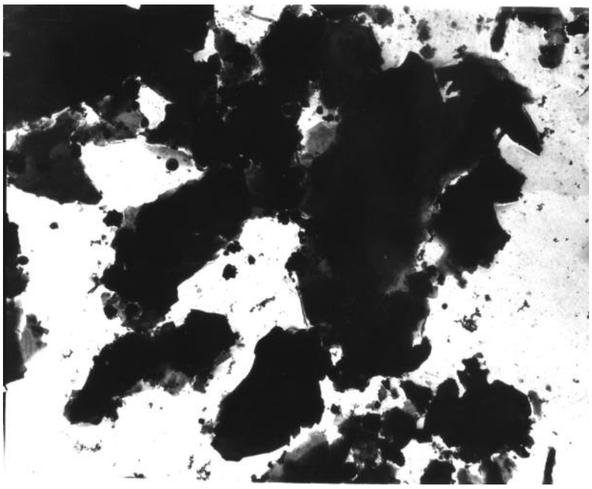

Figure 2. Zone of oxidation of copper and porphyritic deposits: mineral mixture of montmorillonite, kaolinite, halloysite, electronic microphotography, suspension, increased 30 400x

Figure 3. Zone of oxidation of copper and molybdenum and porphyritc deposits: molybdite, electronic microphotography, suspension, increased 30 400x

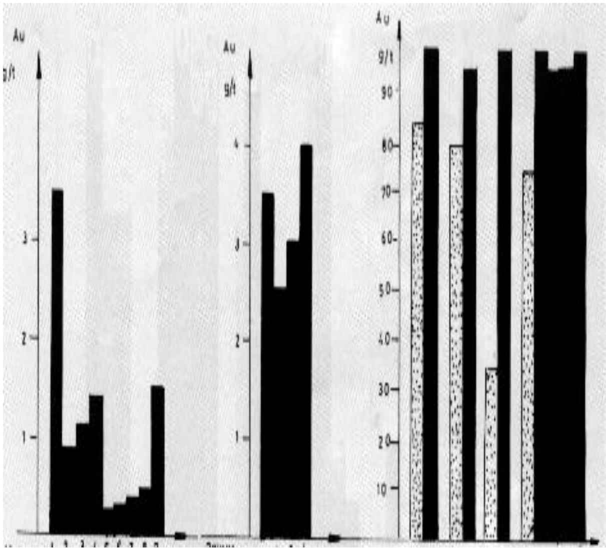

Figure 4. Gold contents in: left – zones of oxidation of copper deposits: Elshitza, Radka, Krassen, Chelopech, Tzar Assen, Assarel, Elatzite, Petelevo (from left to right); middle- terraces of the rivers: Banska Luda Yana, Luda Yana, Topolnitza (Panagiursko), Malak Iskar (Etropolsko) (from left to right); right – gold content (from…to…) of deposits of Radka, Chelopech, Elatzite of river, Banska Luda Yana, Topolnitza, Zlatishka, Malak Iskar (from left to right).

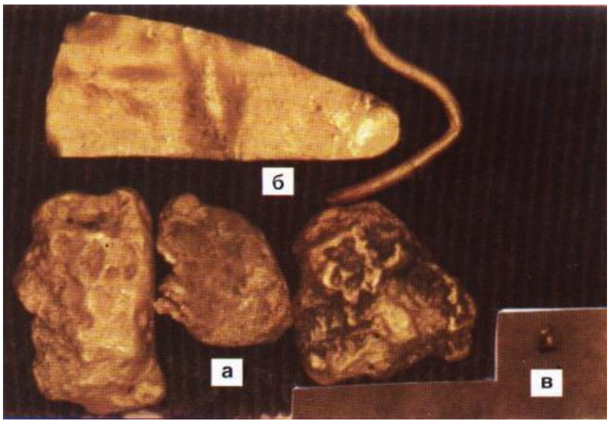

Figure 5. Gold from: a) - terrace of the river of Banska Luda Yana: composition: Au=98,50%; Cu=0,74%;Fe=0,70%; b) - cuttings of juwelleric gold found in the river of Banska Luda Yana, composition: Au=81,40%; Ag=17,11%; Cu=0,79%; Fe=0,70%; c) - zone of oxidation of copper and pyrite deposit "Elshitza", composition: Au=80,40%; Ag=19,60%, increased 5x.

There composition corresponds to gold content from the river terraces in this region (fig. 4). That gives us ground to accept that the main source of deposition of wash gold in the region are infact the zones of oxidation of copper mineralizations. It is of high mill test. The river terrace gold in its composition is close to the gold in the juwelleric cuttings found in the local rivers. Therefore in ancient times gold in the region of Panaguiriste has been extracted from river terraces. Articles of art such as the " Golden treasure of Panaguiriste" have been produced.

Supergenic mineralization are the first geological objects we meet. Comparable mineralogical analysis shows the common features in their mineralogical characteristics. Differences in quantitative deposition of supergenic minerals as well as in their mineral composition have also been established. These mineralogical characteristics are typical for the zones of oxidation found directly on the earth surface. For instance, considerable deposition of hematite, goethite, chalcodone, alum, melanterite, yarosite, gypsum, chalotrichite is typical for copper and pyrite type of deposits. Quantitative deposition of kaolinite, halloysite, hydromica, montmorillonite, mineral mixture "limonite", alunite, chalcanthite, brochantite, secondary staged- copper, malachite, azurite is typical for the zones of oxidation of copper and porphyritic types of deposits. It is rare to find minerals such as: nacrite, ferri and methahalloysite, chalcotrichite, maghemite, scorodite, andrusit, thenardite, antlerite, spangolite. Ferrous hydroxides and oxides, specularite, malachite, azurite are deposits in the zones of oxidation of copper and molybdenum and porphyritic deposits, as well as the typical for them: zincite, claudenite, fluellite, hematolite, libethenite, mimetite, atelestite, chalcophyllite, molybdite, feromolybdite, alunogen, linarite, rosenite, szomolnokite.

The discussed supergenic mineral associations can be considered a reliable critereon in prospecting and exploring new copper deposits in the region. The copper type deposit in depth can be determined by the mineral composition of the earth surface zones of oxidation.

Mineralogical characteristics of supergenic mineralizations give the chance of industrial utilization of these valuable mineral raw materials for copper, gold, kaoline, alum and ochre production. Moreover, present investigations contribute the study of the Central Srednogorie deposits as well as the copper- pyrite and copper- porphyritic and copper-molybdenum- porphyritic genetic types of deposits all over the world.

REFERENCES

Tokmakchieva M., 1981, Some data about the supergenic minerals of the "Elatzite", Jubil. Session 20 years of HIMG, 199-206.

Tokmakchieva M., D.Draganov, 1983, On mineralogy of the zone of oxidation of "Tzar Assen" deposit, S, journal "Rudodobiv", 3., 2-7.

Tokmakchieva M., 1983, On quantitative distribution of supergenic minerals in the zone of oxidation of copper and porphyritic deposits of Panagiursko- Etropolski region, S, journal "Rudodobiv", 10, 6-11.

Tokmakchieva M., 1985, First malachite juvelliric sort deposit in Bulgaria, S, BAN Proc., 2, 207-209.

Tokmakchieva M., D. Draganov, 1985, On the mineralogy of the zone of oxidation of "Elatzite" deposit, S, journal "Rudodobiv", 3., 24-27.

Tokmakchieva M., 1988, Modern mineralization in open- cast mining of copper ores, S, Annual of HVMG, 209-218.

Tokmakchieva M., 1997, Typomorphic mineral composition, of zones of weathering of copper ores, journal "GMR", 1, 17-21.

Tokmakchieva M., 1994, Mineral composition, geochemical characteristics and genesis of copper mineralizations of Panagiursko-Etropolski ore region, publ. ASI. Ltd., S, 458p.

Afanasieva E., M. Isaenko,1981, Determinator of supergenic minerals of oxidized sulphide ores under reflected light, M. Nedra, 133 p.

Smirnov S., 1951, Zone of oxidation of sulphide deposits,M., publ. AN USSR 334p.

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