EVOLUTIONARY SERIES OF AG-CONCENTRATING MINERALS IN EPITHERMAL DEPOSITS OF NORTHEASTERN RUSSIA

N.E. Savva, A.A. Plyashkevich (North-East Interdisciplinary Scientific Research Institute, 16 Portovaya St., Magadan 685000, Russia)

ABSTRACT

Epithermal deposits in Northeastern Russia are major sources of Ag. Understanding of mineralogical and geochemical characteristics of Ag-concentrating minerals has both scientific and practical significance. Numerous investigations demonstrated that, at early stages of ore mineralization, Ag concentrated predominantly in Fe, As, Cu, Pb, Sn, Sn sulphides as isomorphic admixtures and dispersed inclusions. At later stages discrete silver minerals appeared, showing an evolutionary trend of sequential increase in local Ag-bearing capacity of Ag-mineral species. Ag-Sb sulphosalts and freibergite, being arranged in evolutionary series according to the higher content of Ag, have a major role among Ag-concentrating minerals. In addition to general characteristics, evolutionary series acquire individual features related to the geochemical specialization of ores (Ag-Sn, Ag-Cu, Ag-Fe, etc.).

The region shows three major geochemical profiles of near-surface deposits which produced commercial Ag concentration, i.e. Ag-Pb-Zn, Sn-Ag, Au-Ag: (1) Among Ag-concentrating minerals in early paragenetic sequences, Ag-Pb-Sb sulphosalts are widely developed in Ag-Pb-Zn deposits; (2) in Sn-Ag deposits - hocartite in early paragenetic sequences and canfieldite in the later ones; (3) in Au-Ag deposits - in the first place there are compounds of Ag and Au - electrum and küstelite.

Ore formation with high-silver concentrating minerals and native silver prevailing is the result of a long-term (multistage) mineralization at any of the cited types of deposits. A silver-acanthite type of mineral deposit is one of the attributes of a large-scale mineralization.

The epithermal deposits in northeastern Russia are the major sources of silver. The three geochemical profiles of epithermal silver deposits of the region are Ag-Pb-Zn, Au-Ag, and Sn-Ag (Fig. 1).

Fig.1.Scheme of disposition of epithermal Ag-deposits in northeastern Russia. (On the basis of geological materials of Belyi, 1994 with suplements)

1- Siberian craton; Verkhoyano-Chukotskaya province of Mezozoic folding: 2 - median massifs, 3 - Yano-Kolymskaya and Chukotskaya miogeosynclines, 4 - Alazeisko-Öloyskaya eugeosyncline, 5 - marginal rift zones; 6 - Koryaksko-Kamchatskaya province of Cenozoic folding; volcanic provinces: 7 -Paleozoic kedonskaya seriya; Late Mezozoic belts: 8 - Uyandino-Yasachninsky, 9 - Kurvinsky and Oloysko-Alazeisky, 10 -Okhotsk-Chukchi; epithermal Ag-deposits: 11 - Au-Ag, 12 -Sn-Ag, 13 - Ag-Pb-Zn. Numbers in map: Ag-deposits: 1 - Agan, 2 - Agatovskoe, 3 - Abkitskoe, 4 - Ametistovoe, 5 - Arman-skoe, 6 - Aryllakh, 7 - Baimskoe, 8 - Valunistoe, 9 - Vesen-



nee, 10 - Gay, 11 - Golzovoe, 12 - Dazitovoe, 13 - Dukat, 14 - Karamken, 15 - Kegaly, 16 - Kolkhida, 17 - Kubaka, 18 - Kunarevo, 19 - Kavralianskoe, 20 - Mars, 21 - Mechta, 22 - Malyi Ken, 23 - Mshistoe, 24 - Nyavlenga, 25 -Nevskoe, 26 - Oira, 27 - Olcha, 28 - Pepenveem, 29 - Promezhutochnyi, 30 - Pravaya Vizualnaya, 31 - Sentyabrskoe, 32 - Sedoy, 33 - Sergeevskoe, 34 - Silnyi, 35 - Sopka Rudnaya, 36 - Sfaleritovoe, 37 - Teploe, 38 - Tidid, 39 -Tikhoe, 40 - Tokichan, 41 - Ugryumyi, 42 - Urultun, 43 - Utesnoe, 44 - Finish, 45 - Fluoritovyi, 46 - Khakandzha, 47 - Khalaly, 48 - Shirokoe, 49 - Shkolnoe, 50 - Evenskoe, 51 - Junyi, 52 - Ircha, 53 - Dzulietta, 54 - Lunnoe.

Complex volcanogenic small-deep Ag-containing mineralization is connected with some epochs of tectonic and magmatic activities and developed on different substrates. The most ancient Devonian-Carboniferous

mineralization on the Archean-Proterozoic basement was developed on the area of the Omolon craton terrane. The Kubaka deposit is a striking representative of such mineralization (Savva, Vorcepnev, 1990). P.P. Lychagin et al. (1989) distinguished the Later Jurassic-Neocomian epoch on the continental shelf of the Omulevka and Urultun subterranes where a number of Ag-containing epithermal deposits, formed on the Lower Paleozoic basement, occur. The Kunarevka ore complex and Urultun Au-Ag deposit are distinguished among them.



Fig.2 Level of Ag concentration in sulphides for ores from epithermal deposits.

The majority of silver deposits is connected with the Late Mesozoic mineralization of the East-Asia-Arctic belt of magmatic arc deposits, which was formed on the Triassic-Jurassic basement. Large or areas with silver deposits, such as Dukat, Karamken, Palyavaam, Tocichan and others, known from publications, are found (Boyle et. al., 1986; Homich et al., 1989; Mineralogy and origin features, 1992; Sketches on metallogeny, 1994). Later, we shall show the effect of the duration of the formation period and substratum of volcanic structure on the specific character of spectrum of Ag-concentrating minerals.

Numerous investigations demonstrated that at the early stages of ore mineralization, silver concentrated predominantly in Fe, As, Sb, Pb, Zn, and Sn sulphides (Pavlov, 1972; Savva, 1992). In Ag-Pb-Zn deposits, silver concentrates in galena (100-1000 g/t), sphalerite (10-150 g/t), chalcopyrite (200-450 g/t), fahlore (from 500 g/t to 5-8%), and Pb-Sb sulphosalts (100-5000 g/t); in Sn-Ag deposits, in arsenopyrite (10-500 g/t), Pb-Sb sulphosalts (100-1000 g/t), stannite (50-2000 g/t), and chalcopyrite (10-

200 g/t); and Au-Ag deposits, in pyrite (200-1500 g/t), chalcopyrite (100-1000 g/t), galenite (100-500 g/t), and sphalerite (200-1500 g/t), (Fig. 2). In later stages, proper minerals forms of silver appeared, and the evolutionary trend has been a sequential increase of local Ag-bearing capacity of minerals species (Fig. 3). Ag-Sb sulphosalts and Ag-containing fahlores, arranged in evolutionary series according to the higher content of silver, has a major role among Ag-concentrating minerals. Ag mineral species form in the following general sequence.

Ag-Pb-Zn deposits

Complex Pb-Bi-Sb-Ag sulphosalts + freibergite (with low content of silver) \rightarrow Ag-Sb sulphosalts (Ag-50%) - Ag-Sb sulphosalts (Ag-up to 70%) + acanthite + Ag selenides \rightarrow native silver.

Sn-Ag deposits

Freibergite (with low Ag content) \rightarrow freibergite (with high content of Ag) + Ag-Sb sulphosalts + AgS sulphostannates \rightarrow acanthite + selenium-containing phases of Ag minerals \rightarrow native silver.

Au-Ag deposits

Freibergite (with low content of Ag) + Ag-Sb and Ag-As sulphosalts (Ag - up to 50%) + native Au (Ag - 30-40%) \rightarrow Ag-Sb and Ag-As sulphosalts (Ag-up to 75%) + acanthite \rightarrow Ag selenides + native silver (Au - 3-5%) (Savva, 1991; 1992).

In addition to general characteristics, evolutionary series acquire individual features related to the geochemical specialization of ores. Sn specialization of silver ores is connected usually with the inherited petrochemical composition of volcanic structures from Sn-bearing intrusions that is, determined by a high content of Li, B, and Sn in ores (Plyashkevich, Pristavko, 1992).

Silver deposits of the Dukat ore district in the Balygychan-Sugoiski region show such inherited composition. In the Dukat deposit, a high concentration of Sn in sulphides and wide distribution of B-bearing minerals, axinite and bustamite, is noted. The surrounding Ag-Pb-Zn deposits contain stannite, hocartite, canfieldite (Plyshkevich, 1986, 1990, 1992). In the ores Karamken Au-Ag deposits (Arman volcanic structure) Ag sulphostannate (canfieldite) is common, in the lower horizons-acicular cassiterite, that may be the attribute of the tin-porphyry mineralization (Nekrasova, 1972; Eremin, 1974).

Fig. 3 Graphs of successive deposition of Ag-minerals in ores. 1-minerals amounts: a) small; b) great;

c) very small; 2 - stages of mineralization; 3 - evolutionary trend.

Baimskoye, Navlenginskoye, Sergeevskoye Au-Ag deposits, where mineralization is closely related with copper-porphyry magmatic rocks, may serve as the example of Cu specialization. Side by side with common Ag-concentrating minerals, Cu-Ag pyrites (stromeyerite, jalpaite, mackinstryite) appear, and chalcopyrite content increases in the ores of these deposits.

In deposits being formed on the ancient substratum, the genetic relations with the source of substance, determining geochemical specialization, is not always obvious. So, in the Olcha volcanogenic Au-Ag deposit, located on the Omolon craton terrane, ores are enriched in chalcopyrite and mackinstryite is common among Ag-concentrating minerals, but volcanic products contain no high concentrations of Cu. Therefore, we can only hypothesize, that Proterozoic rocks (cupriferous sandstone and siltstone horizons), lying in the basement of volcanic structures. could be the source of Cu (Fig. 4).

We have run down metal supply from the basement rocks on the Omolon craton terrane in Ag-Pb-Zn

Au-Ag deposits N. 199.0 wich. 1974) m7 100 tion ation Sn-Ag deposits Maltii Ke Tokichar 19791 1997 1986) (Plyashkeyich, 1990) Ag-concentration ralbargh Pyrarghti Ì. Ĩ Ag-Pb-Zn deposits Kunarevo 1080 Ag-concentration

deposits, located in the basins of Russkaya Omolonskaya and Pravaya Vizualnaya Rivers in volcanites of the devonian age. The absolute age of lead in galenite of Ag-bearing veins was determined to be 767 and 1577 Ma correspondingly (Shpikerman, 1993). Spectrum analysis showed Pb-300 g/t and Zn-200 g/t concentrations in unchanged ordovician limestones in the environs of the Sedoi deposit, and Pb-150 g/t and Zn-150 g/t concentrations in the Proterozoic calcareous sandstones of the Pravaya Visualnaya river basin.

Multistage regime of the deposit formation caused repeated substance redistribution in rocks, underlying volcanic edifice, its activation, redepositions and concentration in ores of the Devonian age. These facts prove the hypothesis about the involvement of basement substance in volcanogenic mineralizations. It is interesting, that the relatively long-term process of deposit formation gave rise to a high ore differitation in silver, up to the formation of native silver and its large nuggets (850 g). Under hypergene conditions these deposits supply native silver to placers (Pavlov et al., 1986).

The prevailing forms of Ag-concentrating minerals in ores are connected with the duration of formation of the epithermal Ag deposits. As it was already notes, deposits with a long history of evolution are more

diffentiated by silver, i.e. high argentiferous minerals species of Ag prevail in them (fig. 4). Such a regularity was observed not only in Paleozoic volcanogenic Ag deposits but also in the Mesozoic ones. Within the East-Asia-Arctic belt of magmatic arcs deposits, volcanogenic Ag deposits occur, which were formed under the conditions of the Early Cretaceous volcanic activity; and in the Late Cretaceous, their ore-containing structures were intruded by juvenile magmatic formations. The intrusion stage corresponded to the stage of the ongoing development of deposits and caused regeneration, recrystallization, and the redeposition of substance of the early stage and its interaction with the introduced substance of the later stage.

Omolon massif		Omulevka height
D e posits		
Sedoy	Olcha	Shirokoe
(Ag-Pb-Zn)	(Au-Ag)	(Ag-Pb-Zn)
Main Ag-minerals in ores		
shtembergite	mackinstryite	owyheete
Ag Fe ₂ S ₃	Ag Cu S	Ag2Pb5Sb6S16
.≌ prustite	jalphaite	freibergite
Ag3As S3	Ag ³ CuS ⁵	(Ag.Cn)10 Zn2Sb4S14
Ag3As S3	Aggeusz	(AZ.S.II)10 ZII2304314
Ag, Sb, S	Ag, Sb, S	Ag, Sb, S
(Fe,Co, Ni)Asz PbS	CuFeS ₂ CuFeS ₂	Pb S ZnS
$\binom{335}{K_2}$	515155 / D2-3	155555
rhyolite	andezite	rhyolite
	าโนการแก้นการแก้งกินกินกินกินกินกินกินกินกินกินกินกินกินก	
Fe, Ni, Co, As	Cu	Pb, Zn, S
	ann inn ann suitheann	uunu <mark>nunnin (</mark> uunninnin
ទ្ធ រព្រារពារពាររីពារពារពារពារ	และและเกิดสาวที่เกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิดการเกิด	
y y Jaspheroides O	metamorphic rocks	limestones
0 2	AR- PT	Pz
Co - 60 g/t		
Ni - 40 g/t	stratiformed - Cu?	
As - 70 g/t	monzonitoides	Pb-Zn skams
Pb-300g/t; Zn-200g/t		

Fig.4 Schematic metal supply from the rock basement.

The Dukat deposit (unique in its structure and history of geologic evolution), which has large reserves and has no analogous in the world, may serve as a striking examples of the described history of evolution. This deposit is situated in the Omsukchan riftogenous zone and located in a volcanic-intrusive dome, composed of extrusive sheets and bodies of fine- and mediophyric and aphyric high-potassic rhyolites, felsorhyolites, and iguinimbrites of the Early Cretaceous age (Kopytin, 1990). Subvolcanic bodies and dikes of biotite rhyolites, granite porphyries, and nevadites of the Late Cretaceous age are widely distributed. Wells at the depth of 1000-1300 m undercuts the Late Cretaceous subvolcanic granites, similar in petrochemical composition with granitoids of the Okhotsk complex. Their Rb-Stages are 82 ± 4 Ma. The formation of the deposit is a complex and longterm process: its early stage is connected with volcanogenic activity, and the later one with the pluton sequence is intrusion. This determined in metasomatities and mineral ore paragenesis (Sidorov et al., 1978; Naiborodin, Savva, 1981). The early stage

includes silification, adularization, and hydromicatization of country rocks and formation first of silverpolysulphide and then quartz-adular-chlorite paragenesis of ores. The later stage includes hematitization and epidotization of country rocks, formation in the country rock mass of granite-magnetite lenses and flat veins of rhodonite-rhodochrosite composition with helvite and garnet, crossing the veins of the early paragenesis.

More than 80 ore-mineral species occur in veins and vein zones. The most common are: pyrite, galenite, sphalerite, chalcopyrite, hematite, pyrolusite, pirargyrite, acanthite and gold-containing native silver (3-15 wt% Au). Acanthite and native silver prevail among silver minerals, and the deposit is of silver-acanthite mineral type. The principal mineralogic characteristic feature consists in superposition of the later high-temperature paragenesis with skarn helvite-garnet-bustamite association on the early quartz-adular paragenesis in connection with the pluton intrusion. This superposition resulted in thermal metamorphism of the early silver paragenesis, exterminating almost completely silver sulphosalts and Ag-containing fahlores. These minerals (more than 30 species) are poorly distributed minerals in ore deposits. Thermal metamorphism resulted in deposition of high-concentrated Ag compounds, acanthite, and native silver. As the example may serve the deposit Nyavlenga, where Au-Ag mineralization of the Lower Cretaceous age is metamorphosed in connection with the intrusion of the Late Cretaceous granitoids with a pronounced copper-molybdenum geochemical specialization (Petrov, 1994). As in the Dukat deposit, superposition had an effect on metasomatites and ores that resulted in the prevalence of acanthite and native silver among Ag-concentrating minerals. Owing to Cu supply, a wide variety of Cu-Ag pyrites appear, although their part in the reserve balance is not very important.

We can say with certainty that the silver-acanthite minerals type is one of the attributes of a large-scale mineralization, because the prevalence of Ag-containing minerals of high concentration shows the completeness of the evolutionary series of Ag-concentrating minerals and a high extent of differentiation in silver content. In conclusion, we want to emphasize once more that, besides widely known characters of a large-scale

mineralization-multistage process and ore metamorphism-calling for the long-term geological investigation, it is possible to make the similar preliminary estimation immediately in the lump of ore from the prevailing Agconcentrating minerals.

ACKNOWLEDGEMENTS

This work is supported by the program, "Evolutionary Species-Formation of Ag-Minerals." The authors wish to acknowledge the program sponsors, Russian Fund Fundamentals of Investigation. We are particularly grateful to Dr. M.L. Gelman, Prof. V.F. Belyi, and Dr. V.I. Shpikerman for their help and consultations.

REFERENCES

Boyle, R.V., 1979. The Geochemistry of Gold and Its Deposits (together with a chapter on geochemical prospecting for the element). - Geol. Surv. Canada Bull. 280, 585 p.

Boyle, E., Ffaser, S., Riz, R., 1986. Silver Natural Resources Forum. - United Nations 10 (4): 331-341.

Belyi, V.F., 1994. Geology of the Volcanogenic Belt. - Magadan: NEISRI FEB RAS. 76 p. (in Russian).

Eremin, R.A., 1974. Gidrotermalny Metamorfizm I Orudenenie Armanskoj Vulkanostruktury. - N-k: Nauka. 134 p. (in Russian).

Gulevich, V.V., 1974. Subvulcanicheskie Obrazovania I Orudenenie V Basseine R. Baimki. - Mat. Geol. i Pol. Iscop. SV SSSR 21: 108-116. (in Russian).

Homich, V.G., Ivanov, V.V., Fotianov, I.I., 1989. Tipizacia Au-Ag Orudenenia. - Vadivostok: DVO AN SSSR. 292 p. (in Russian).

Kopytin, V.I., 1990. Sn-Ag Rudnie Formacyi Balygychano-Suboiskogo Progiba. - In: Metallogenia I Rudnie Formacyi Zony Perehoda Kontient-Okean. Magadan: NEISRI FEB RAS: 158-173. (in Russian).

Lychagin, P.P., Dylevsky, E.F., Shpikerman, V.I., Likman, V.B., 1989. Magmatizm Centralnyh Raionov Severo-Vostoka SSSR. - Vladivostok: DVO AN SSSR. 120 p. (in Russian).

Nagornaya, T.V., 1979. Sulfosoly serebra na olovorudnom mestorozhdenie. - In: Mineralogiya serebra blizpovekhnostnykh mestorozhdeny: 56-59 (in Russian).

Naiborodin, V.I., Savva, N.E., 1981. Vozrastnye Vzaimootnoshenia Mineralov V Rudah Vulkanogennyh (Epitermalnyh) Au-Ag Mestorozdeni. - In: Mineraly, Gornie Porody I Mestorozdenia Poleznih Iskopaemyh V Geologicheskoy Istories. L.: Nauka: 45-46. (in Russian).

Nekrasov, I.J., 1984. Mineralnie Associacie Mestorozdeni Sn-Ag Formacie Severo-Vostoka SSSR. - Mineral. J. 6 (3): 74-86. (in Russian).

Nekrasova, A.N., 1972. Osobennosti mineralnogo sostava rud Karamkenskogo Au-Ag mesto rozdenia. - Geol. rudn. mestor. 3: 45-54. (in Russian).

Parilov, J.S., 1972. Geohimicheskie tipy serebrosoderzaschih mestorozdeniy. - Geol. rudn. mestor. 14 (2): 40-55. (in Russian).

Pavlov, G.F., Savva, N.E., Horin, G.I., Teplyh, V.I., Tovma, I.T., Dzarihin, K.G. Buliakov, G.H., 1986. Samorodnoe serebro v rossypiah Severo-Vostoka SSSR. - In: Mineraly i mineralnie paragenezisy porod i rud Severo-Vostoka SSSR. Magadan: NEISRI FEB RAS: 77-89. (in Russian).

Plyashkevich, A.A., 1986. Sravnitelnaya mineralogiya kassiterit-silikatnogo i serebro-polimetallicheskogo mestorozdeni (Omsukchansky raion, Magadanskoy oblasti). - In: Mineraly i mineralnie paragenezisy porod i rud Severo-Vostoka SSSR. Magadan.: NEIRSI FEB RAS: 115-129. (in Russian).

Plyashkevich, A.A., 1990. O kanfilditovom tipe olovo-serebro-polimetallicheskogo orudenenia. - In: Rudnie formacie Severo-Vostoka SSSR. Magadan: NEIRSI FEB RAS: 141-151. (in Russian).

Plyashkevich, A.A., 1992. Mineralogia serebra olovo-serebro-polimetallicheskih mestorozdeni (Severo-Vostok Rossiy). -In: Mineralogia i geohimia rudnyh poley Severo-Vostoka Rossiy. Magadan.: NEIRSI FEB RAS: 11-24. (in Russian).

Plyashkevich, A.A., Pristavko, V.A., 1992. Sistematizacia olovorudnyh mestorozdeni po ih serebronosnosti. -In: Mineralogia i geohimia rudnih poley Severo-Vostoka Rossiy. Magadan.: NEISRI FEB RAS: 63-39. (in Russian).

Savva, N.E., 1991. Princip sistematiki mineralov serebra . - In: Teoreticheskaya mineralogia 1: 47-48. (in Russian).

Savva, N.E., 1992. Differencialnye riady mineralov serebra v serebrosoderjaschih prirodnyh sistemah. - In: Mineralogia i geochimia rudnyh poley Severo-Vostoka Rossiy. Magadan: NEIRSI FEB RAS: 3-11. (in Russian).

Savva, N.E., Vedernikov, V.N., 1989. Novie tip serebrianoy mineralizaciy na Severo-Vostoke SSSR. - In: Geohimia i mineralogia rudnih mestorojdeny Severo-Vostoka SSSR. Magadan: NEIRSI FEB RAS: 86-97. (in Russian).

Savva, N.E., Vorcepnev, V.V., 1990. Osobennosti formirovania vulkanogennyh mestorojdeniy na sredinnyh massivah. -

In: Genezis rudnyh formaciy i prakticheskoe znachenie rudnoformacionnogo analiza na Severo- Vostoke SSSR. Magadan.: NEIRSI FEB RAS: 50-64. (in Russian).

Shilo, N.A., Sakhorova, M.S., Krivitskaya, N.N., Riakhovskaya, S.K., Bryzgalov, I.A., 1992. Mineralogy and Origin Features of Gold-Silver Ores of the North-East Part of Pacific Ocean Frame. - M.: Nauka. 256 p. (in Russian).

Sidorov, A.A., 1966. Zoloto-serebrianoe orudenenie Centralnoy Chukotki. - M.: Nauka. 146 p. (in Russian).

Sidorov, A.A., and N.A. Goraychev (Eds.) Sketches on metallogeny and geology of mineral deposits in Northeastern Russia. - Magadan: NEIRSI FEB RAS. 105 p. (in Russian).

Sidorov, A.A., Goryachev, N.A., Shpicerman, V.I., Savva, N.E., Eremin, R.A., Pristavco, V.A., Gorodinsky, M.E., Bjalobdzessky, S.G., 1994. Sketches on metallogeny and geology of mineral deposits in Northeastern Russia. Magadan: NEIRSI FEB RAS. 106 p. (in Russian).

Sidorov, A.A., Konstantinov, M.M., Eremin, R.A., Savva, N.E., Korytin, V.I., Safronov, D.N., Naiborodin, V.I., Goncharov, V.I., 1989. Serebro (geologia, mineralogia, genezis, zakonomernosti razmeschenia mestorojdenie). - M.: Nauka. 240 p. (in Russian).

Shpikerman, V.I., Chernyshov, I.V., Agapova, A.A., Troickey, V.A., 1994. Geglogia izotopov rudnogo svinca centralnih raionov Severo-Vostoka Rossie. - Magadan: NEIRSI FEB RAS. 36 p. (in Russian).

•