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Specific Composition of Native Silver from the Rogovik Au–Ag Deposit, Northeastern Russia

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Abstract—The first data on native silver from the Rogovik Au–Ag deposit in northeastern Russia are presented. The deposit is situated in central part of the Okhotsk–Chukchi Volcanic Belt (OCVB) in the territory of the Omsukchan Trough, unique in its silver resources. Native silver in the studied ore makes up finely dispersed inclusions no larger than 50 μm in size, which are hosted in quartz; fills microfractures and interstices in association with küstelite, electrum, acanthite, silver sulfosalts and selenides, argyrodite, and pyrite. It has been shown that the chemical composition of native silver, along with its typomorphic features, is a stable indication of the various stages of deposit formation and types of mineralization: gold–silver (Au–Ag), silver–base metal (Ag–Pb), and gold–silver–base metal (Au–Ag–Pb). The specificity of native silver is expressed in the amount of trace elements and their concentrations. In Au–Ag ore, the following trace elements have been established in native silver (wt %): up to 2.72 S, up to 1.86 Au, up to 1.70 Hg, up to 1.75 Sb, and up to 1.01 Se. Native silver in Ag–Pb ore is characterized by the absence of Au, high Hg concentrations (up to 12.62 wt %), and an increase in Sb, Se, and S contents; the appearance of Te, Cu, Zn, and Fe is notable. All previously established trace elements—Hg, Au, Sb, Se, Te, Cu, Zn, Fe, and S—are contained in native silver of Au–Ag–Pb ore. In addition, Pb appears, and silver and gold amalgams are widespread, as well as up to 24.61 wt % Hg and 11.02 wt % Au. Comparison of trace element concentrations in native silver at the Rogovik deposit with the literature data, based on their solubility in solid silver, shows that the content of chalcogenides (S, Se, Te) exceeds saturated concentrations. Possible mechanisms by which elevated concentrations of these elements are achieved in native silver are discussed. It is suggested that the appearance of silver amalgams, which is unusual for Au–Ag mineralization not only in the Omsukchan Trough, but also in OCVB as a whole, is caused by superposition of the younger Dogda–Erikit Hg-bearing belt on the older Ag-bearing Omsukchan Trough. In practice, the results can be used to determine the general line of prospecting and geological exploration at objects of this type.

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INTRODUCTION

Native silver is a widespread mineral at Au–Ag deposits of the Okhotsk–Chukchi Volcanic Belt (OCVB) in northeastern Russia. These are the well-known high-grade deposits: Dukat, Karamken, Dal'neye, Kvartsevaya Sopka, Irbychan, Oroch, Lunnoe, Arylakh, Primorskoe, Dzhul'etta, and other objects, where native silver is the basic ore mineral, whereas at such a silver giant as the Dukat deposit, it is the major ore mineral (Konstantinov et al., 1998, 2003; Ryzhov et al., 2000; Struzhkov and Konstantinov, 2005). Despite this, much less attention is paid to native silver as compared with gold. Only its dimensions, morphology, and mineral assemblages have been studied (Posukhova, 1978; Berman and Struzhkov, 1980; Yushko-Zakharova, 1986; Sidorov et al., 1989; Shilo et al., 1992; Konstantinov et al., 1998; Sakharova et al., 1998; Filimonova et al., 2003, 2006; Filimonova and Trubkin, 2004; Spiridonov and Yanakieva, 2012). There were a relatively few publications that consider the chemical composition of native silver, e.g., (Berman and Struzhkov, 1980; Novgorodova, 1983; Sakharova et al., 1983; Shilo et al., 1992; Konstantinov et al., 2003).

We have decided to fill this gap by studying the chemical composition of native silver at the Rogovik Au–Ag deposit. Earlier studies (Kravtsova et al., 2012, 2015, 2016; Zhuravkova et al., 2015; Palyanova et al., 2015; Kravtsova and Makshakov, 2016) pointed out the promise of the chosen object for solving this question. It should be emphasized that the study of the composition of native silver, quantitative estimation of trace elements therein, and revealing of their possible occurrence is done for the first time.

In practice, all Au–Ag deposits, as well as silver deposits proper, are the basis of such an important branch of Russia's national economy as mining and processing of silver ore. Some Au–Ag deposits, especially large and unique ones, are complex systems, the evolution and origin of which span long time intervals, and silver makes a substantial contribution to the total reserves. In studying such deposits, interest in native silver is obvious.

It should be noted that according to the rules adopted by the International Mineralogical Association (IMA), there are two mineral species, native silver (with an Ag content higher than 50 wt % and fineness of 0–500‰, in mole fractions $Ag_{0.65-1}Au_{0.35-0}$) and native gold (with Ag content up to 50 wt % and fineness of 500–1000‰ in mole fractions $Ag_{0-0.65}Au_{1-0.35}$). Characterizing native silver and gold, we, however, adhere to the terminology adopted in early publications (Petrovskaya et al., 1976a, 1976b; Boyle, 1979; Petrovskaya, 1993): native silver, $Ag_{1.0}Au_{0.0}$–$Ag_{0.94}Au_{0.06}$ (0–100‰); küstelite, $Ag_{0.94}Au_{0.06}$–$Ag_{0.85}Au_{0.15}$ (100–250‰); electrum, $Ag_{0.85}Au_{0.15}$–$Ag_{0.44}Au_{0.56}$ (250–700‰); high-fineness gold, $Ag_{0.44}Au_{0.56}$–$Ag_{0.0}Au_{1.0}$ (700–1000‰).

With respect to native silver and gold containing mercury, various terms are accepted: mercurous silver, mercurous gold, intermetallides, or stoichiometric silver and gold compounds and silver and gold amalgams. Below, we use term amalgams of silver and/or gold with respect to double and triple natural solid solutions and stoichiometric compounds of silver and/or gold with mercury.

CHARACTERIZATION OF THE DEPOSIT

The Rogovik Au–Ag deposit is located at the periphery of the central OCVB at the northern closure of the Omsukchan Trough (Kuznetsov et al., 1992), which is unique in its metallogenic specialization for silver (Kuznetsov and Livach, 2005; Struzhkov and Konstantinov, 2005; Sidorov et al., 2009, 2011; Sidorov and Volkov, 2015). This territory borders on ore-bearing structures in eastern Yakutia, one of which is represented by the younger Dogda–Erikit mercurous belt in the rear zone of the older Cretaceous OCVB (Spikerman and Goryachev, 1996; Gamyanin et al., 2003). In administrative terms, Rogovik is located in Magadan oblast and is included in the Omsukchan ore district, which is the largest in gold and silver reserves (Fig. 1, inset). The information on structural position, geological structure, chemical and phase compositions of rocks and ores is given by (Kuznetsov et al., 1992; Kravtsova et al., 2012, 2015, 2016; Zhuravkova et al., 2015; Palyanova et al., 2015; Kravtsova and Makshakov, 2016). Geological exploration of this area was carried out incompletely, and its outlook remains unclear.

The deposit is hosted in intensely argillized volcanic and sedimentary rocks of the Lower Cretaceous Omsukchan Formation. Rhyolitic vitroclastic and ash tuffs with interlayers of polymictic tuffaceous breccia predominate (Figs. 1a, 1b). According to our previous study, the ore mineralization at the Rogovik deposit formed during two stages (Kravtsova et al., 2012, 2015). The typical epithermal low-sulfide gold–silver ore proper is related to the early volcanic stage. The substantially *silver mineralization* (conventionally silver–base-metal type of ore) formed at the later volcanic–plutonic stage under the action of granitoid magmatism. In areas of juxtaposed gold–silver (Au–Ag) and silver–base-metal (Ag–Pb) mineralization, a gold–silver–base-metal (Au–Ag–Pb) ore multiformation in composition formed.

Au–Ag Ore

Au–Ag ore is predominant at the upper levels in the central part of deposit and is represented by northwest-trending zones of adularia–quartz and hydromica–adularia–quartz veins and vein zones (Fig. 1b). Banded and colloform ore textures are typical. Pyrite is predominant among simple sulfides. Silver minerals—acanthite, proustite, pyrargyrite, and küstelite—are widespread; naumannite and native silver are less abundant. Gold is mainly represented by electrum (639–673‰). The gold–acanthite mineral assemblage with selenides in adularia–quartz veins is the most productive. The chemical composition of ore comprises (ppm): up to 6.04 Au, up to 40 Ag, up to 800 As, up to 50 Sb, up to 15.8 Se, and up to 2.7 Hg. Only Au and Ag make up ore. A S content less than 1 wt % is typical of low-sulfide Au–Ag ore.

Ag–Pb Ore

Ag–Pb ore consists of sericite–quartz and sericite–orthoclase–quartz veinlets. They are largely localized at middle depths and crosscut the Au–Ag ore in the northeastern direction (Fig. 1b). Thin and short veins with massive and brecciated textures are sporadic. The most abundant ore minerals are sulfosalts (proustite, pyrargyrite, stephanite), selenides (S-naumannite), Se-acanthite, and silver amalgams, as well as sternbergite, stromeyerite, polybasite, polyargyrite, miargyrite, tennantite, tetrahedrite, and freibergite. Chalcopyrite, sphalerite, and galena, along with pyrite, represent simple sulfides. The most productive is the Ag-sulfosalt assemblage with selenides in zones of sericite–quartz veinlets, which is distinguished by high-Hg native silver. Silver is the major useful component; its concentration reaches 1000 ppm or higher. High contents have also been established for Hg (up to 46.5 ppm), Se (up to 132.8 ppm), As (up to 600 ppm), Sb (up to 200 ppm), and B (up to 300 ppm). Increased contents are also characteristic of Cu (up to 100 ppm),

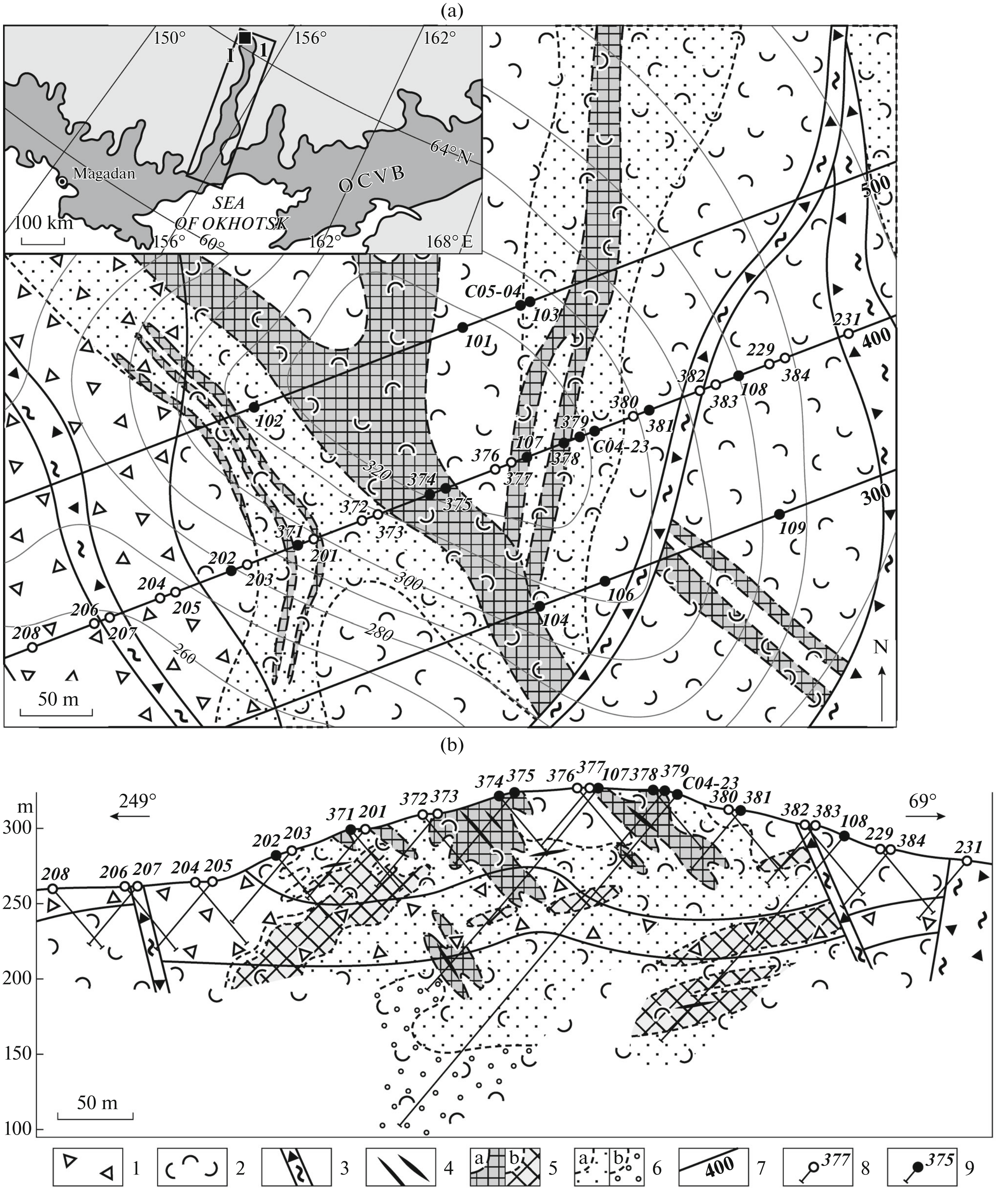

Fig. 1. Schematic geological map of central part of Rogovik Au–Ag deposit (a) and schematic geological section along reference profile 400 (b). Compiled by authors using data of Dukat Geological Exploration Enterprise, Magadan. (1, 2) Lower Cretaceous volcanic–sedimentary sequence (Omsukchan Formation): (1) tuffaceous breccia, (2) rhyolitic vitroclastic and ash tuffs; (3) crush and foliated zones; (4) quartz and quartz–feldspathic veins; (5) zone of intense mineralization: (a) Au–Ag veins and veinlets, (b) Ag–Pb stringers; (6) zone of stringer–disseminated mineralization: (a) Ag–Pb and (b) Au–Ag–Pb; (7) profile and its number; (8) borehole and its number; (9) borehole, from which mineralogical and geophysical large-volume samples have been taken. Inset: Okhotsk–Chukchi volcanic belt (OCVB): (I) Omsukchan ore district, (1) Rogovik Au–Ag deposit.

Pb (up to 300 ppm), and Zn (up to 400 ppm). The S content increases up to 15.4 wt %.

Au–Ag–Pb Ore

Au–Ag–Pb ore frequently appears with depth as zones of veinlets, silicification, and sulfidation (Fig. 1b). Stringer–disseminated sulfide mineralization (pyrite, arsenopyrite) is hosted in argillized metasomatic rocks. The small veinlets are composed of quartz, sericite, adularia (orthoclase), and carbonate. Albite and chlorite also occur. The stringer–disseminated structure was formed by filling of open fissures and by metasomatic replacement of rocks and ores. All aforementioned minerals and chemical elements are identified here. The amount of simple sulfides—pyrite, galena, chalcopyrite, and sphalerite—becomes more abundant. Some sulfide veinlets are similar in mineral and chemical compositions to the Ag–Pb ore, which is widespread in the Omsukchan Trough like the Au–Ag ore (Kalinin et al., 1984; Sidorov et al., 1989; Kravtsova et al., 1996, 1998; Plyashkevich, 2002; Konstantinov et al., 2003; Struzhkov and Konstantinov, 2005; Kravtsova, 2010). Hessite, argyrodite, imiterite, and silver amalgams appear as well, although they are more typical of silver ore. The most productive is the gold–silver–polysulfide mineral assemblage with sulfosalts, selenides, and silver amalgams hosted in zones of quartz–adularia (orthoclase)–carbonate veinlets. The highest contents of Ag (up to 10000 ppm), Zn (up to 2000 ppm), Pb (up to 1000 ppm), Cu (up to 1000 ppm), Se (up to 684.6 ppm), Sb (up to 600 ppm), and Hg (up to 168 ppm) are established precisely here. Ge (>100 ppm), Te (up to 27 ppm), and Bi (up to 15 ppm) also occur here. Au is distributed extremely nonuniformly, from <0.02 to 260 ppm. The sulfur content increases up to 18.3 wt %.

RESEARCH METHODS

Silver minerals were studied under a Micromed Polar-3 polarizing microscope. About 80 large-volume mineralogical–geochemical samples of borehole cores have been taken from ore intervals in various sections and units of the Rogovik deposit (Fig. 1). After their analysis for a wide range of elements and after petrographic examination of polished sections, the selected ore materials containing silver minerals and native silver were set into six briquette polished cartridges with several dozen grains in each cartridge.

Later, the composition of native silver grains were studied with a JXA-8200 microanalyzer equipped with wave and EX-84055MU energy dispersive spectrometers (JEOL Ltd., Japan). The study was performed at the Vinogradov Insitute of Geochemistry, Siberian Branch, Russian Academy of Sciences, in Irkutsk using techniques elaborated by Pavlova and Paradina (1990) and Pavlova and Kravtsova (2006). Taking into account the low stability of Ag minerals under the action of an electron beam, we selected the optimal conditions for excitation and recording of the analytical signal, as well as recalculation of the recorded X-ray radiation intensity to the concentrations of Ag, Au, Hg, Sb, As, Se, S, and other chemical elements. It has been shown that quantitative determination of the elemental silver mineral composition is possible at the surface density of the electron flux, which does not exceed 2.55 μW/μm^2.

To further study the native silver composition, we also used a MIRA 3 LMU SEM (Tescan Orsay Holding) equipped with the INCA Energy 450+ microanalysis system and an INCA Wave 500 wave spectrometer (Oxford Instruments Nanoanalysis Ltd., USA). The study was performed at the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, in Novosibirsk. The time of spectra acquisition was 15–20 s; Ag, Au–Ag alloys, $CuFeS_2$, PbSe, ZnS, Sb_2S_3, and As_2S_3 were used as standards. The detection limits of elements were tenths of a percent. The uncertainty in determining the basic components (>10–15 wt %) does not exceed 1% and <2% for components with concentrations of 1–10 wt %.

In all cases, quantitative measurements are estimated for grains no less than 5 μm in size, in order to avoid background amounts of elements occurring in the adjacent phases. The minimum diameter of beam is 1 μm.

RESULTS

In contrast to native gold, native silver occurs in all types of ore and its chemical composition, along with the size and morphology of grains and mineral assemblages, is a peculiar characteristic indicating the mineralogical, geochemical, and genetic features of the revealed mineralization.

Au–Ag Ore

The native silver in this type of ore is relatively rare. Its Au-bearing variety—küstelite—is predominant. The native silver more frequently makes up micro- and fine-dispersed inclusions in quartz (Fig. 2); fills microfractures and interstices in this main gangue mineral often in association with küstelite, Se-akanthite, silver sulfosalts (proustite, pyrargyrite) and naumannite; and occasionally corrodes and replaces minerals in intergrowths. It is noteworthy that native silver microinclusions are frequently identified within küstelite and electrum of lower fineness. The size of native silver grains usually does not exceed 10 μm. Round grains frequently with zonal internal structure are predominant. Au, Hg, Sb, Se, and S are constant trace elements. The contents of these elements are relatively low and hardly exceed 2 wt % (Table 1).

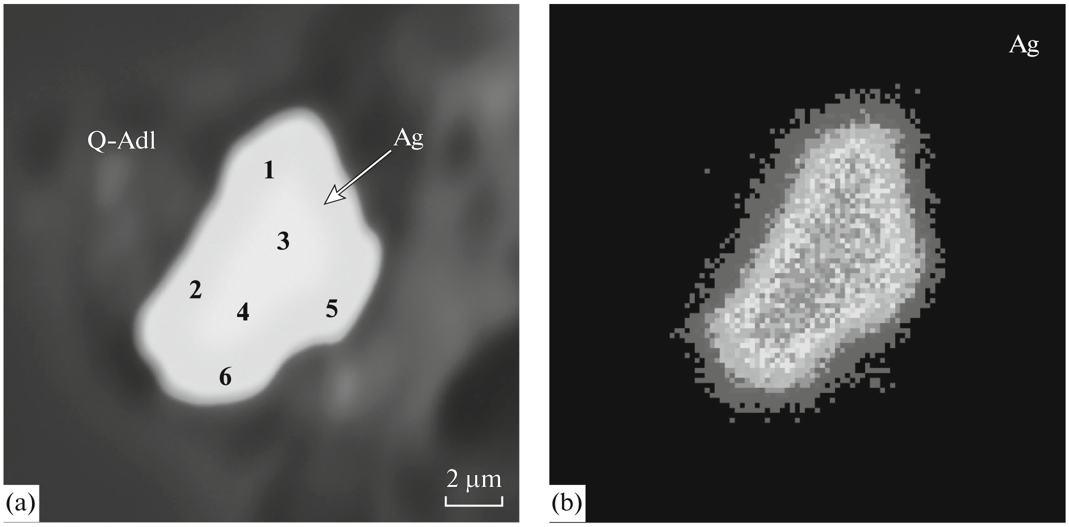

Fig. 2. Interstitial segregation of native silver (Ag) in quartz–adularia (Q–Adl) veinlet 6 × 10 µm in size. Images: (a) BSE, (b) in X-ray of Ag; 1–6 in photo are points of elements determination shown in Table 1 (grain 1).

Sulfur is an exception. Its content and character of distribution in zonal grains (Fig. 2; Table 1, grain 1) are noteworthy. At the margin of a grain (points 1, 2, 5, 6), the level of the S concentration varies from 2.10 up to 2.72 wt %. Trace elements (Au, Hg, Sb, Se) occur constantly. At the center of a grain, S concentration does not exceed 1.66 wt % (points 3, 4), and other trace elements are not detected. It should be emphasized that the grain being measured is associated only with quartz and adularia. Other minerals that can be seen with a microscope were not revealed.

Table 1. Results of X-ray spectral microanalysis (wt %) of native silver (grains 1–4). Au–Ag ore. Rogovik deposit

n	Ag	Au	Hg	Sb	Se	S	Total	Mineral formula*
				Grain 1				
1	96.31	0.12	1.27	0.39	0.59	2.72	101.40	$Ag_{0.897}Hg_{0.006}Au_{0.001}[S_{0.085}, Se_{0.008}, Sb_{0.003}]$
2	96.50	0.18	0.98	0.46	0.45	2.62	101.19	$Ag_{0.902}Hg_{0.005}Au_{0.001}[S_{0.082}, Se_{0.006}, Sb_{0.004}]$
3	98.77	<0.12	<0.20	<0.14	<0.16	1.12	99.89	$Ag_{0.963}[S_{0.037}]$
4	97.89	<0.12	<0.20	<0.14	<0.16	1.66	99.55	$Ag_{0.946}[S_{0.054}]$
5	96.08	0.21	1.46	0.56	0.19	2.10	100.60	$Ag_{0.918}Hg_{0.007}Au_{0.001}[S_{0.067}, Sb_{0.005}, Se_{0.002}]$
6	94.55	0.31	1.32	0.68	0.22	2.65	99.73	$Ag_{0.898}Hg_{0.007}Au_{0.002}[S_{0.084}, Sb_{0.006}, Se_{0.003}]$
				Grain 2				
1	96.85	<0.12	0.81	1.74	0.26	1.18	100.84	$Ag_{0.939}Hg_{0.004}[S_{0.039}, Sb_{0.015}, Se_{0.003}]$
2	96.71	<0.12	0.53	1.18	1.01	0.74	100.17	$Ag_{0.949}Hg_{0.003}[S_{0.024}, Se_{0.014}, Sb_{0.010}]$
				Grain 3				
1	96.87	0.89	1.70	0.51	<0.16	1.08	101.05	$Ag_{0.946}Hg_{0.009}Au_{0.005}[S_{0.036}, Sb_{0.004}]$
2	95.08	1.86	1.50	0.41	<0.16	1.21	100.06	$Ag_{0.938}Au_{0.010}Hg_{0.008}[S_{0.040}, Sb_{0.004}]$
				Grain 4				
1	96.86	<0.12	0.95	1.75	0.49	0.22	100.27	$Ag_{0.966}Hg_{0.005}[Sb_{0.015}, S_{0.007}, Se_{0.007}]$
2	96.70	0.16	0.89	1.74	0.55	0.21	100.25	$Ag_{0.964}Hg_{0.005}Au_{0.001}[Sb_{0.015}, Se_{0.008}, S_{0.007}]$

As, Te, Cu, Pb, Zn, Ni, Co, Fe, W, Mo, Sn, Bi, Ge, Mn are not detected. Here and in Tables 2–4: *n* are points of determination. Here and in Tables 2, 3, the results are obtained with electron probe JXA-8200 microanalyzer (JEOL Ltd., Japan); in Table 4 the results are obtained with SEM MIRA 3 LMU (Oxford Instruments Nanoanalysis Ltd., USA).

* Here and in Tables 2, 3: in square brackets trace elements can enter silver and/or occur in the form of a mechanical admixture of proper phases.

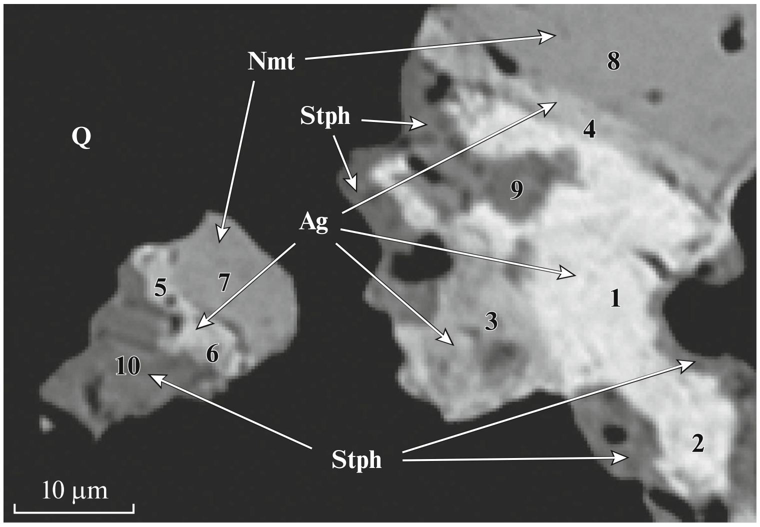

Fig. 3. Xenomorphic aggregate consisting of native silver and silver amalgams (Ag), naumannite (Nmt), and stephanite (Stph) in quartz (Q). 1–10 in photo are points of elements determination shown in Table 2 (grains 5, 6). BSE image.

In general, the composition of trace elements in native silver and their relatively low concentrations rather distinctly reflect the geochemical features of the Au–Ag type of mineralization proper. Like in ore, the almost complete geochemical profile of elements-indicators is recorded in native silver. Along with S, these are Au (up to 1.86 wt %), Hg (up to 1.70 wt %), Sb (up to 1.75 wt %), and Se (up to 1.01 wt %).

Ag–Pb Ore

Native silver most frequently occurs in association with stephanite, naumannite, and silver amalgams (Fig. 3; Table 2, grains 5, 6) in the form of intergrowths with Se-acanthite, less frequently with silver sulfosalts (pyrargyrite and myrargyrite) and fahlore (freibergite and tetrahedrite). Native silver makes up micro- and finely dispersed inclusions in quartz and pyrite (Fig. 4; Table 2, grains 10, 11). Still less abundant native silver is associated with other ore minerals, e.g., sternbergite, stromeyerite, galena, and sphalerite.

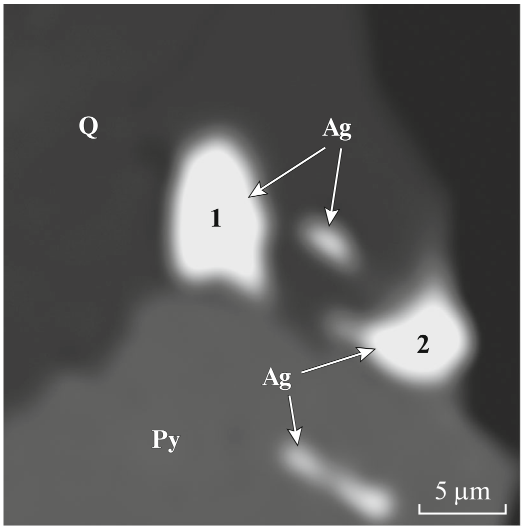

Fig. 4. Finely dispersed native silver (Ag) in association with quartz (Q) and pyrite (Py). 1, 2 in photo are points of elements determination shown in Table 2 (grains 10, 11). BSE image.

Grains irregular in shape are characteristic of native silver; they are mainly included in xenomorphic aggregates consisting of silver sulfosalts, naumannite, and quartz. As a rule, the size of these grains rarely exceeds 30 µm. As for simple sulfides, native silver is most frequently associated with pyrite. Small clotted and spongy particles of native silver are noted on acanthite crystals. In individual cases, they are encountered as sheets along the cleavage in galena. Fine silver inclusions along fractures in sphalerite occur even more rarely. Hg, Sb, and Se have been established as constant trace elements in native silver; Cu and S are often noted; Te, Zn, and Fe appear as well (Table 2, grains 5–9). The amount of trace elements and their concentrations in native silver increase appreciably compared to Au–Ag ore.

The absence of Au admixture, high Hg concentrations, increase in Sb, Se, and S contents, and the appearance of Te, Cu, Zn, and Fe are the main distinguishing typomorphic indications of native silver in Ag–Pb ore. Native silver frequently occurs as xenomorphic aggregates; dimensions of particles vary from finely dispersed (<10 µm) to small (10–30 µm), and the relative diversity of mineral assemblages is evidence for a more complex multicomponent composition of ore-forming systems and various physicochemical conditions during the formation of Ag–Pb mineralization compared to Au–Ag.

Table 2. Results of X-ray spectral microanalysis (wt %) of native silver, silver amalgam, naumannite, and stephanite (grains 5–11). Ag–Pb ore. Rogovik deposit

n	Ag	Hg	Sb	Se	Te	Cu	Zn	Fe	S	Total	Mineral formula
Silver amalgam (grain 5)											
1	89.34	11.13	<0.14	<0.16	<0.20	<0.10	<0.10	<0.05	0.33	100.80	$Ag_{0.926}Hg_{0.062}[S_{0.012}]$
2	87.63	10.93	<0.14	<0.16	<0.20	0.34	<0.10	<0.05	0.40	99.30	$Ag_{0.918}Hg_{0.062}[S_{0.014}, Cu_{0.006}]$
3	96.74	2.49	1.14	0.34	<0.20	<0.10	<0.10	<0.05	0.25	100.96	$Ag_{0.964}Hg_{0.013}[Sb_{0.010}, S_{0.008}, Se_{0.005}]$
4	95.51	0.66	<0.14	2.04	<0.20	0.28	<0.10	<0.05	1.44	99.93	$Ag_{0.919}Hg_{0.003}[S_{0.047}, Se_{0.027}, Cu_{0.004}]$
Native silver (grain 6)											
5	96.14	1.45	1.34	0.64	<0.20	<0.10	<0.10	<0.05	0.45	100.02	$Ag_{0.956}Hg_{0.008}[S_{0.015}, Sb_{0.012}, Se_{0.009}]$
6	96.96	0.94	1.48	1.35	<0.20	<0.10	<0.10	<0.05	0.71	101.44	$Ag_{0.941}Hg_{0.005}[S_{0.023}, Se_{0.018}, Sb_{0.013}]$
Naumannite (grains 5, 6)											
7	76.42	0.15	<0.14	21.44	<0.20	<0.10	<0.10	<0.05	2.11	100.12	$(Ag_{2.031}, Hg_{0.002})_{2.033}(Se_{0.778}, S_{0.189})_{0.967}$
8	76.63	0.14	<0.14	20.15	<0.20	<0.10	<0.10	<0.05	2.12	99.04	$(Ag_{2.064}, Hg_{0.002})_{2.066}(Se_{0.742}, S_{0.192})_{0.934}$
Stephanite (grains 5, 6)											
9	68.01	0.18	14.85	1.42	<0.20	<0.10	<0.10	<0.05	15.89	100.35	$(Ag_{4.977}, Hg_{0.007})_{4.984}Sb_{0.963}(S_{3.911}, Se_{0.142})_{4.053}$
10	68.65	<0.20	15.25	0.42	<0.20	<0.10	<0.10	<0.05	16.09	100.41	$Ag_{5.018}Sb_{0.987}(S_{3.953}, Se_{0.042})_{3.995}$
Silver amalgam (grain 7)											
1	96.42	2.14	<0.14	1.02	<0.20	0.22	<0.10	0.28	<0.15	100.08	$Ag_{0.965}Hg_{0.012}[Se_{0.014}, Fe_{0.005}, Cu_{0.004}]$
2	96.14	2.65	0.34	0.64	<0.20	<0.10	<0.10	<0.05	<0.15	99.77	$Ag_{0.974}Hg_{0.014}[Se_{0.009}, Sb_{0.003}]$
Silver amalgam (grain 8)											
1	86.72	12.62	0.82	0.27	<0.20	0.32	<0.10	<0.05	<0.15	100.75	$Ag_{0.911}Hg_{0.071}[Sb_{0.008}, Cu_{0.006}, Se_{0.004}]$
2	94.58	4.85	0.72	0.18	<0.20	0.15	<0.10	<0.05	<0.15	100.48	$Ag_{0.962}Hg_{0.027}[Sb_{0.006}, Cu_{0.003}, Se_{0.002}]$
Silver amalgam (grain 9)											
1	84.93	4.14	3.39	1.11	1.29	1.84	0.55	1.14	1.77	100.16	$Ag_{0.809}Hg_{0.021}[S_{0.057}, Cu_{0.030}, Sb_{0.029}, Fe_{0.021}, Se_{0.014}, Te_{0.010}, Zn_{0.009}]$
2	83.92	6.21	1.28	1.05	1.30	1.95	0.57	1.09	1.70	99.07	$Ag_{0.815}Hg_{0.032}[S_{0.056}, Cu_{0.032}, Fe_{0.020}, Se_{0.014}, Sb_{0.011}, Te_{0.011}, Zn_{0.009}]$
Native silver (grain 10)											
1	99.85	<0.20	<0.14	<0.16	<0.20	<0.10	<0.10	<0.05	<0.15	99.85	Ag
Native silver (grain 11)											
2	99.92	<0.20	<0.14	<0.16	<0.20	<0.10	<0.10	<0.05	<0.15	99.92	Ag

Au, As, Pb, Ni, Co, W, Mo, Sn, Bi, Ge, Mn are not detected.

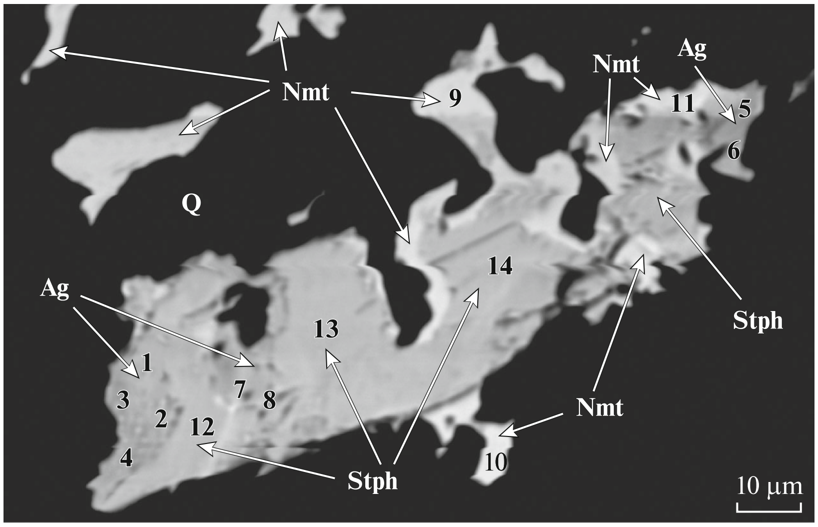

Fig. 5. Xenomorphic aggregate consisting of native silver (Ag), naumannite (Nmt) and stephanite (Stph) in quartz (Q). 1–14 in photo are points of elements determination shown in Table 3 (grain 12). BSE image.

Au–Ag–Pb Ore

Native silver in this ore commonly occurs in association with acanthite, silver sulfosalts (mainly stephanite), naumannite, and argyrodite (Figs. 5, 6; Tables 3, 4) and frequently replaces and rims them. Microinclusions of native silver particles are noted in electrum and küstelite. The grains tend to grow and regenerate. Native silver grains 50 μm in size or more predominate. Zonal structures complicated by various heterogeneities are rather common.

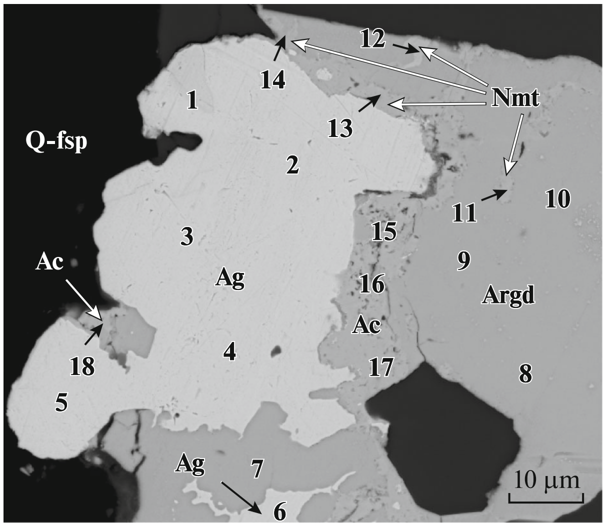

Fig. 6. Xenomorphic aggregate consisting of silver and gold amalgams (Ag), argyrodite (Argd), naumannite (Nmt), and acanthite (Ac) in quartz–feldspatic (adularia, orthoclase) aggregate (Q-fsp). 1–18 in photo are points of elements determination shown in Table 4. BSE image.

The composition of trace elements and their concentrations in native silver typical of this ore (Tables 3, 4) are extremely variable and in general reflect their complex and unstable formation conditions. Almost all of the aforementioned chemical elements, Au, Hg, Sb, Se, Te, Cu, Zn, Fe, and S, have been established; Pb appears (up to 1.58 wt %). The stark distinguishing feature characterizing this type of mineralization is widespread silver amalgams containing up to 24.6 wt % Hg and 11 wt % Au (Table 3, grains 13 and 14; Table 4, grain 16).

DISCUSSION

The results show that native silver in various ores of the Rogovik deposit is characterized by different trace elements and their variable concentrations. The typical chemistry of native silver is distinctly expressed in its qualitative and quantitative compositions. In general, the composition of trace elements in native silver and the level of their concentrations reflect sufficiently well the geochemical features of each of the studied ore types (Au–Ag, Ag–Pb, Au–Ag–Pb) (Kravtsova et al., 2015; Kravtsova and Makshakov, 2016). The almost complete geochemical profile of elements indicators of mineralization is present: Au, Hg, Sb, Se, and S for Au–Ag ore (Table 1); Hg, Sb, Se, Te, Cu, Zn, Fe, and S for Ag–Pb ore (Table 2); Au, Hg, Sb, Se, Te, Cu, Pb, Zn, Fe, and S for Au–Ag–Pb ore (Tables 3, 4).

The heterogeneities in composition and diverse occurrence of trace elements in native silver are evidence for unstable physicochemical conditions of ore formation and indicate manifold and consecutive deposition of silver and accompanying elements in the course of mineral formation. The Hg contents are especially indicative of this. They vary even within one

Table 3. Results of X-ray spectral microanalysis (wt %) of native silver, silver amalgam, naumannite, acanthite, and stephanite (grains 12–15). Au–Ag–Pb ore. Rogovik deposit

n	Ag	Au	Hg	Sb	Se	Te	Cu	Pb	Zn	Fe	S	Total	Mineral formula
Native gold (grain 12)													
1	94.72	<0.12	<0.20	0.64	2.91	<0.20	<0.10	<0.15	<0.10	<0.05	2.30	100.57	$Ag_{0.886}[S_{0.072}, Se_{0.037}, Sb_{0.005}]$
2	94.70	<0.12	<0.20	0.54	2.84	<0.20	<0.10	<0.15	<0.10	<0.05	2.26	100.34	$Ag_{0.888}[S_{0.071}, Se_{0.036}, Sb_{0.004}]$
3	99.29	<0.12	<0.20	<0.14	0.19	<0.20	<0.10	<0.15	<0.10	<0.05	0.50	99.98	$Ag_{0.981}[S_{0.017}, Se_{0.002}]$
4	99.20	<0.12	<0.20	<0.14	0.37	<0.20	<0.10	<0.15	<0.10	<0.05	0.45	100.02	$Ag_{0.980}[S_{0.015}, Se_{0.005}]$
5	96.64	0.62	0.22	<0.14	<0.16	<0.20	<0.10	1.05	<0.10	0.26	1.38	100.17	$Ag_{0.940}Au_{0.003}Hg_{0.001}[S_{0.045}, Pb_{0.005}, Fe_{0.005}]$
6	95.07	1.39	0.35	<0.14	<0.16	<0.20	1.62	<0.15	<0.10	<0.05	2.02	100.45	$Ag_{0.901}Au_{0.007}Hg_{0.002}[S_{0.064}, Cu_{0.026}]$
7	98.30	<0.12	<0.20	0.84	<0.16	<0.20	<0.10	<0.15	<0.10	0.08	1.55	100.77	$Ag_{0.941}[S_{0.050}, Sb_{0.007}, Fe_{0.002}]$
8	95.03	1.09	1.20	<0.14	<0.16	<0.20	0.49	1.58	<0.10	<0.05	1.93	101.32	$Ag_{0.910}Hg_{0.006}Au_{0.006}[S_{0.062}, Cu_{0.008}, Pb_{0.008}]$
Naumannite (grain 12)													
9	76.91	<0.12	<0.20	<0.14	21.00	<0.20	<0.10	<0.15	<0.10	<0.05	1.30	99.21	$Ag_{2.098}(Se_{0.783}, S_{0.119})_{0.902}$
10	76.12	<0.12	<0.20	<0.14	22.55	<0.20	<0.10	<0.15	<0.10	<0.05	1.58	100.25	$Ag_{2.035}(Se_{0.823}, S_{0.142})_{0.965}$
11	62.89	<0.12	<0.20	<0.14	34.61	<0.20	0.66	<0.15	<0.10	<0.05	0.35	98.51	$(Ag_{1.678}, Cu_{0.030})_{1.708}(Se_{1.261}, S_{0.031})_{1.292}$
Stephanite (grain 12)													
12	67.89	<0.12	<0.20	14.78	0.99	<0.20	<0.10	<0.15	<0.10	<0.05	14.83	98.49	$Ag_{5.135}Sb_{0.990}(S_{3.773}, Se_{0.102})_{3.875}$
13	68.42	<0.12	<0.20	14.35	1.05	<0.20	<0.10	<0.15	<0.10	<0.05	15.73	99.55	$Ag_{5.050}Sb_{0.938}(S_{3.906}, Se_{0.106})_{4.012}$
14	68.08	<0.12	<0.20	15.10	<0.16	<0.20	<0.10	<0.15	<0.10	<0.05	15.91	99.09	$Ag_{5.044}Sb_{0.991}S_{3.965}$
Silver amalgam (grain 13)													
1	91.50	1.12	7.20	0.24	<0.16	<0.20	<0.10	<0.15	<0.10	<0.05	<0.15	100.06	$Ag_{0.952}Hg_{0.040}Au_{0.006}[Sb_{0.002}]$
2	88.62	0.62	10.20	0.16	<0.16	<0.20	<0.10	<0.15	<0.10	<0.05	<0.15	99.60	$Ag_{0.937}Hg_{0.058}Au_{0.004}[Sb_{0.001}]$
Silver amalgam (grain 14)													
1	85.12	2.25	12.57	<0.14	<0.16	<0.20	<0.10	<0.15	<0.10	<0.05	<0.15	99.94	$Ag_{0.914}Hg_{0.073}Au_{0.013}$
2	82.15	3.12	18.25	<0.14	<0.16	<0.20	<0.10	<0.15	<0.10	<0.05	<0.15	100.40	$Ag_{0.893}Hg_{0.107}$
Native silver (grain 15)													
1	99.01	<0.12	<0.20	<0.14	<0.16	0.25	<0.10	<0.15	0.20	<0.05	0.60	100.06	$Ag_{0.975}[S_{0.020}, Zn_{0.003}, Te_{0.002}]$
2	99.05	<0.12	<0.20	<0.14	<0.16	0.28	<0.10	<0.15	0.42	<0.05	<0.15	99.75	$Ag_{0.991}[Zn_{0.007}, Te_{0.002}]$

As, Ni, Co, W, Mo, Sn, Bi, Ge, Mn are not detected.

Table 4. Results of X-ray spectral microanalysis (wt %) of silver and gold amalgams, argyrodite, naumannite, and acanthite (grain 16). Au–Ag–Pb ore. Rogovik deposit

n	Ag	Au	Hg	Se	Te	Cu	Pb	Fe	Ge	S	Total	Mineral formula
Silver and gold amalgams												
1	77.28	7.88	14.26	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	99.42	$Ag_{0.866}Hg_{0.086}Au_{0.048}$
2	76.32	9.65	15.15	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	101.12	$Ag_{0.850}Hg_{0.091}Au_{0.059}$
3	66.78	10.59	24.60	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	101.97	$Ag_{0.778}Hg_{0.154}Au_{0.068}$
4	64.73	9.12	24.61	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	98.46	$Ag_{0.780}Hg_{0.160}Au_{0.060}$
5	67.32	8.03	23.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	98.55	$Ag_{0.800}Hg_{0.148}Au_{0.052}$
6	77.70	11.02	10.69	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	99.41	$Ag_{0.868}Au_{0.068}Hg_{0.064}$
Argyrodite												
7	76.87	<0.20	<0.20	1.10	<0.20	<0.20	<0.20	<0.20	5.89	15.75	99.61	$Ag_{8.230}Ge_{0.936}(S_{5.673}, Se_{0.161})_{5.834}$
8	74.86	<0.20	<0.20	4.80	<0.20	<0.20	<0.20	<0.20	5.48	13.86	99.00	$Ag_{8.246}Ge_{0.896}(S_{5.136}, Se_{0.722})_{5.858}$
9	76.66	<0.20	<0.20	3.09	<0.20	<0.20	<0.20	<0.20	6.35	13.11	99.21	$Ag_{8.555}Ge_{1.052}(S_{4.922}, Se_{0.471})_{5.393}$
10	75.29	<0.20	<0.20	4.39	<0.20	<0.20	<0.20	<0.20	5.52	13.46	98.66	$Ag_{8.380}Ge_{0.912}(S_{5.040}, Se_{0.668})_{5.708}$
Naumannite												
11	73.53	<0.20	<0.20	21.88	1.39	<0.20	<0.20	1.20	<0.20	1.44	99.44	$(Ag_{1.974}, Fe_{0.062})_{2.036}(Se_{0.802}, S_{0.130}, Te_{0.032})_{0.964}$
12	75.71	<0.20	<0.20	22.51	<0.20	1.16	<0.20	0.70	<0.20	1.53	101.61	$(Ag_{1.976}, Cu_{0.052}, Fe_{0.035})_{2.063}(Se_{0.803}, S_{0.134})_{0.937}$
13	74.11	<0.20	<0.20	24.96	<0.20	<0.20	<0.20	0.42	<0.20	0.49	99.98	$(Ag_{2.009}, Fe_{0.022})_{2.031}(Se_{0.924}, S_{0.045})_{0.969}$
14	74.08	<0.20	<0.20	21.11	1.14	<0.20	<0.20	0.52	<0.20	1.81	98.66	$(Ag_{2.003}, Fe_{0.027})_{2.030}(Se_{0.780}, S_{0.164}, Te_{0.026})_{0.970}$
Acanthite												
15	82.79	<0.20	<0.20	1.19	<0.20	<0.20	<0.20	<0.20	1.32	13.59	98.89	$(Ag_{1.880}, Ge_{0.045})_{1.925}(S_{1.038}, Se_{0.037})_{1.075}$
16	83.89	<0.20	<0.20	3.84	<0.20	<0.20	2.57	<0.20	<0.20	11.24	101.54	$(Ag_{1.962}, Pb_{0.031})_{1.993}(S_{0.884}, Se_{0.123})_{1.007}$
17	84.34	<0.20	<0.20	5.16	<0.20	<0.20	<0.20	<0.20	<0.20	11.20	100.70	$Ag_{1.960}(S_{0.876}, Se_{0.164})_{1.040}$
18	82.94	<0.20	<0.20	2.71	<0.20	<0.20	<0.20	<0.20	<0.20	13.48	99.13	$Ag_{1.885}(S_{1.031}, Se_{0.084})_{1.115}$

As, Sb, Zn, Ni, Co, W, Mo, Sn, Bi, Mn are not detected.

grain from 0.66 to 11.13 wt % (Table 2, grain 5), in certain cases from 10.69 to 24.61 wt % (Table 4, grain 16). Sulfur concentrations vary from 0.21 to 2.72 wt %. In some grains, the sulfur distribution is zonal with an obvious tendency toward enrichment of the marginal zone (Fig. 2 and Table 1, grain 1). Native silver quite often corrodes and replaces the intergrown minerals, in particular, acanthite. Microinclusions of native silver in küstelite and electrum are signs of ore matter redeposition.

The fact that native silver occurs in ore where pyrite is the most abundant mineral (up to 95% of all ore minerals) is evidence for low-temperature ore formation, inasmuch as line of Ag–Ag_2S equilibrium intersects pyrite–pyrrhotite monovariant curve at ~245°C (Taylor, 1970). This implies that metallic silver could have been stable together with pyrite only below this temperature. In addition, the earlier developed thermodynamic analysis of stability conditions of silver sulfoselenides of acanthite series characteristic of the Rogovik deposit indicates a temperature below 110–177°C and low oxygen fugacity, i.e., reductive conditions (Zhuravkova et al., 2015). In our opinion, the reductive conditions, low temperature, and characteristic trace elements, especially sulfur, are key factors of native silver formation at the Rogovik deposit. These factors also control the geochemistry of the native silver.

The constant presence of Hg and its high contents in native silver up to the formation of the high-mercurous variety of this mineral is not typical of Au–Ag mineralization at other deposits of the Omsukchan Trough and OCVB as a whole (Posukhova, 1978; Berman and Struzhkov, 1980; Novgorodova, 1983; Sakharova et al., 1983, 1998; Sidorov et al., 1989; Shilo et al., 1992; Konstantinov et al., 1998, 2003; Filimonova et al., 2003, 2006; Filimonova and Trubkin, 2004; Spiridonov and Yanakieva, 2012). On the one hand, the appearance of silver amalgams in ore of the studied deposit can be explained by the unique metallogenic specialization for silver of the riftogenic Omsukchan Trough (Kuznetsov and Livach, 2005; Struzhkov and Konstantinov, 2005; Sidorov et al., 2009, 2011; Sidorov and Volkov, 2015). On the other hand, it can be suggested that mercurous mineralization is related to the young Dogda–Erikit mercury-bearing belt formed in the rear zone of the Cretaceous OCVB (Shpikerman and Goryachev, 1996; Gamyanin et al., 2003) and its superposition on the older Ag-bearing Omsukchan Trough.

At the Rogovik deposit, silver amalgams have been revealed in Ag–Pb and Au–Ag–Pb ores, and this is evidence for increased Hg activity from early to late stages. Silver amalgam is not characteristic of Au–Ag ore. It should be emphasized that Au–Ag ore at the studied deposit, which started to form at the early volcanic stage, was rejuvenated later, as a result of plutonogenic magmatism activity related to multiple tectonomagmatic activization of the ore district (Berman et al., 1993; Goncharov and Sidorov, 1999). This is confirmed by the zonal distribution of trace elements in native silver (Fig. 2; Table 1, grain 1). Variation of trace element compositions in native silver from almost pure to high-mercurous varieties within the deposit and their variable occurrence indicate manifold and consecutive precipitation of silver in the course of mineral formation at various stages in the evolution of the Rogovik deposit.

Natural silver amalgams in the Ag–Au–Hg system with high silver content are extremely rare. They more frequently contain an admixture of gold (Basu et al., 1981; Healy and Petruk, 1990; Bortnikov et al., 2006; Borisenko et al., 2014; Chudnenko et al., 2015). The Verkhoyansk territory of eastern Yakutia with the adjoining northern part of the Omsukchan Trough and the Rogovik deposit is an exception in this respect. The Nochnoe, Kholodninsky, and Khachakchan deposits, as well as Obokha, Kutekchan, and Shcherbakovsky ore occurrences, have been discovered here. Nuggets of silver amalgam and Ag–Hg intermetallides are revealed in their ores (Krylova and Kichigin, 1989; Konstantinov et al., 2003; Kostin and Denisov, 2007; Kostin et al., 2011). In addition, many ore-bearing structures of this territory are characterized by rather widespread Au–Ag mineralization along with complex base-metal Ag–Pb, Ag–Sb, and Ag–Hg mineralization. Kostin et al. (2011) assume that findings of silver amalgams are a prospecting guide, which points to the probability of high-grade silver mineralization in the area where amalgams are localized.

The concentrations of trace elements established in native silver at the Rogovik deposit are presented in Table 5. The data on the solubility of these elements in solid silver known from the literature are also given for comparison. The Hg, Au, Sb, Cu, Zn, and Pb concentrations do not exceed solubility in solid silver and should be referred to isomorphic (structural) admixtures. For example, the highest Hg concentrations established in silver amalgam of Au–Ag–Pb mineralization do not exceed 24.61 wt % (Table 4, grain 16) or 16 at % (Table 5). These concentrations are within the interval of mercury solubility in solid silver in the Ag–Hg system (Baren, 1996) and in natural silver amalgam with a small amount of gold (Chudnenko and Palyanova, 2013 and references therein). The data on solubility of antimony in Au–Ag solid solution obtained from an experimental study of the Au–Ag–Sb system (Hansen and Anderko, 1958; Zoro et al., 2006) agree with the amount of antimony contained in native silver at various stages of the formation of the Rogovik deposit and do not exceed 3.4 wt % (Tables 1–3) or 2.9 at % (Table 5).

As is known, the solubility of S, Se, and Te in metallic silver is low and corresponds to the first tenth of at % (Table 5). These values cannot explain the contents of these elements, which are revealed in native silver at the Rogovik deposit (Table 1, grains 1–3). The absence of any significant S contents in Ag microinclusions incorporated into the sulfide pyrite matrix (Table 2, grains 7, 8, 10, 11 and Table 4, grain 16) shows that the established admixture of S in Ag in other cases is not an analytical error. One of the possible causes is a uniform, though zonal distribution (Fig. 2, Table 1, grain 1) of nanoparticles of silver (and possibly mercury) sulfides, selenides, and tellurides. Mineral and metallic nanoparticles have recently been detected in various objects and geochemical settings (Filimonova et al., 2003; Deditius et al., 2011).

However, taking into account the chemical activity and inclination toward aggregation of nanoparticles (Gilbert et al., 2003), it is unlikely that their micrometer-size aggregates, even if sporadic, are accessible for SEM observation. Therefore, it is more feasible to discuss another explanation. The intergrowths of native silver with electrum and küstelite are evidence for nonequilibrium processes, because owing to complete miscibility of the components in the Ag–Au system, these parageneses are forbidden. Such a mineral assemblage is thermodynamically forbidden under conditions of complete ("global") equilibria, but it is not in the concept of local equilibrium. Indeed, in experimental modeling and DFT calculations of small clusters of Ag_mS_n, Ag_nAu_mS (Wu et al., 2010; Zhao et al., 2013), it has been shown that certain compositions are thermodynamically preferable to others; i.e., they have a lower free formation energy. Although they are

Table 5. Intervals of trace element contents in native silver at Rogovik deposit as compared with their solubility in solid silver, after literature data*

Element	Content in native silver, at %	Solubility in solid silver, at %
Au	0.1–6.8	100 (compete miscibility)
Hg	0.3–16	37 (45–270°C)
Cu	0.4–3.2	14 (779°C), 1 (400°C)
Zn	0.9–3.6	40.2 (258°C)
Pb	0.5–0.8	0.4 (250°C), 1.5 (400°C)
Fe	0.1–2.1	0.0002 (650°C)
As	Not detcted	4 (300°C), 7.8 (582°C)
Sb	0.1–2.9	5.5 (300°C), 6.2 (340°C)
S	0.5–10.1	0.17
Se	0.2–3.6	0.27
Te	1–1.8	0.005

* Hansen and Anderko, 1958; Elliot, 1970; Glazov and Burkhanov, 1980; *Noble Metals,* 1984; Swartzendruber, 1984; Karakaya and Thompson, 1990; Baren, 1996; Zoro et al., 2006.

nonequilibrium “globally”, they can exist under certain conditions, especially in the case of stabilization by S adsorption. It is quite possible that they may contain other stabilizing elements, such as Se, Te, and Sb.

We have come to these conclusions studying Au–Ag ore of the Kvartsevaya Sopka deposit in northeastern Russia (Tauson et al., 2017). In this case, it was also difficult to explain the appearance of S-bearing spots in electrum and küstelite grains with a uniform distribution of sulfur, but with a significantly lower content of it relative to the known complex Au and Ag sulfides (uytenbogaardtite and petrovskaite) identified in ores of many Au–Ag deposits (Palyanova et al., 2014). Therefore, a suggestion has been proffered about the formation of Ag_nAu_m clusters stabilized by S with its subsequent aggregation into nanoparticles and then into larger agglomerate commensurable with the dimensions of crystallites (blocks) in solid solution. In this case, sulfur will be “trapped” by the boundaries of these blocks (Urusov et al., 1997) and perceived at a resolution accessible to SEM as uniformly distributed. In support of the hypothesis, we note that native silver, including that from the Dukat deposit, frequently has a domain structure and consists of nanocrystals 20–25 nm in size (Spiridonov and Yanakieva, 2012). Thus, we assume that S and partly Se and Te can occur in native silver in the so-called internal adsorption state (Urusov et al., 1997).

The continuing analogy with the Dukat Au–Ag deposit, where specialization for silver is predominant and the ore, like at the Rogovik deposit, is multiformation, the data of (Konstantinov et al., 2003, p. 51) should be quoted. “Many trace elements—gold, mercury, antimony, copper, iron, manganese, beryllium, lead, and zinc—have been identified in native silver from the Dukat deposit. By character of incorporation, the trace elements are subdivided into structural (gold, antimony, mercury) and mechanical (bismuth, copper, iron, manganese, lead, zinc), related to alien microinclusions or surficial films of minerals.” Some quite large objects with similar composition of native silver can be cited. Sakharova et al. (1998) established up to 0.2 wt % Se (Dukat, Kubaka, Karamken deposits) and up to 0.68 wt % Te (Kubaka, Valunistoe deposits) in addition to Au, Hg, Sb, Cu, Pb, Zn, Fe, Bi, and Mn in native silver from Au–Ag deposits of the OCVB.

The results obtained for Sb and As look strange from the viewpoint of solubility in silver. Possessing almost same isomorphic possibilities with respect to both elements (Table 5), silver takes Sb in its composition, but “rejects” As, although abundant Sb and As minerals occur in Au–Ag ore. The revealed relationship with respect to As and Sb is traced in a majority of other Au–Ag objects in the OCVB. For example, despite the extensive diversity of the trace elements (Au, Hg, Sb, Se, Te, Cu, Pb, Zn, Fe, Bi, Mn, Be) revealed at the Dukat, Karamken, Kubaka, and Valunistoe deposits, arsenic was not established therein (Sakharova et al., 1998; Konstantinov et al., 2003). The Rogovik Au–Ag deposit studied by us also has not become an exception, despite the fact that As minerals (proustite, freibergite, As-pyrite, and also arsenopyrite in multiformation ore) are abundant there. In addition, as shown earlier, the correlations between Ag and As are not characteristic not only of native silver, but also of all ores at Au–Ag deposits in the OCVB. We have seen it at Au–Ag deposits of the Evensky group (Dal’neye, Kvartsevaya Sopka, Oroch, Irbychan) and at the Dukat deposit (Kravtsova, 1998, 2010; Kravtsova et al., 2003). The revealed tendency is clearly expressed at both the macro- (ore, halos) and microlevel (minerals). It can be suggested that because both elements occur in the system, they are in principle able to make up solid solutions with Ag (up to 4–5 at % at 300°C), and the lack of As is caused by the aforementioned reductive setting of ore formation, owing to which As occurs in solution as stable sulfide and hydrosulfide complexes; for Sb this is less characteristic.

As for the occurrence of trace elements in native silver as a whole, it can be suggested that they are more diverse in natural processes than it is commonly accepted, dividing them in mechanical and entering into structure of solid solutions. An interesting fact is indirectly supported by the study of ore minerals and metasomatic rocks from the Dukat ore field and deposit of the same name by a group of researchers from the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, in Moscow. Using scanning and transmission electron microscopy, they obtained images of nanoparticles of native Ag, Bi, Pb, Sn, Zn, zincite, and Cu–Zn alloy. The nanoaggregates made up of fibrous native silver, and globular AgS nanoparticles have been established. Nanoparticles consisting of Ag–Bi–Pb–Cd–Cu and Au (Ag–Ni–Fe) compounds have been found by Filimonova et al. (2003), Filimonova and Trubkin (2004), and Sidorov et al. (2012). Thus, it is not ruled out that trace elements in the natural silver are represented by nanosized particles and vary in composition at the Rogovik deposit as well.

CONCLUSIONS

The typical chemistry of native silver, along with general typomorphic features, are expressed at the Rogovik Au–Ag deposit quite distinctly and reflects the geochemical specificity of ore. The chemical composition of native silver is a stable indicator which characterizes the type of ore mineralization. The specificity of native silver is reflected in the quantity of trace elements and their concentrations. Native silver with a simple chemical composition and a low level of trace element concentrations (Au, Hg, Sb, Se, S) are characteristic of the early Au–Ag stage. Native silver of a later stage, when Ag–Pb and Au–Ag–Pb ores are formed, is distinguished by complex, extremely unstable chemical compositions and higher concentrations of trace elements Hg, Sb, Se, S, Cu, Te, Zn, and Fe; Au and Pb additionally appear in Au–Ag– Pb ore.

The rather unusual chemical composition of native silver with its enrichment in Sb and depletion in As is noteworthy; elevated concentrations of S and Se, Ag microinclusions in küstelite and electrum. These features apparently are a consequence of reductive conditions and a low crystallization temperature, as the key factors controlling native silver formation and trace element contents therein. The same conditions are favorable for the origination of uniformly distributed sulfide and selenide nanoparticles, silver sulfoselenides, and small Ag_mS_n, Ag_nAu_m, and Ag_nAu_mS clusters capable of aggregating into nanoparticles and then into larger agglomerates commensurable with the dimensions of crystallites in native silver. Their relative stability can be achieved by means of sulfur adsorption and apparently other stabilizing elements, e.g., Se and Sb.

With respect to the distribution and occurrence of trace elements in native silver, it can be stated that in natural processes they differ by significant diversity from trace elements entering into the structure of solid solutions and compositionally varying ultradispersed and nanosized particles and minerals to aggregates consisting of compounds made up of two or several metals. The formation of relatively pure native silver and silver amalgams provides evidence for increase in Hg activity from early to late stages, as well as for degree and scale of rejuvenation developing here. With allowance for these factors, primary (hydrothermal) and regenerated (hydrothermally redeposited) endogenic silver are distinguished.

In practice, the results can be used for determining the general line of prospecting and geological exploration of similar objects. If we adopt a firm opinion on the viewpoint that silver amalgams are prospecting guides, then we can give a positive assessment of the Rogovik area for revealing new ore deposits, not just gold and silver ones.

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