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ARTICLES

Determination of Precious Metals in Geological Samples from Four Gold Ore Deposits of the North-East of Russia

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Abstract—Compositions of rare mineral phases containing precious metals (PMs) in samples from Natalka, Pavlik, Vetrenskoe, and Degdekan gold ore deposits (North-East of Russia) are studied by scintillation atomic emission spectrometry (SAES) and electron probe microanalysis (scanning electron microscopy and electron probe X-ray microanalysis, SEM–EPMA). The SAES method found dozens and hundreds of particles carrying gold, silver, and all platinum-group elements as native metals, intermetallides and solid solutions, arsenides, antimonites, sulfoarsenides, tellurides, selenides, etc. The variety of the elemental compositions of PM species (mineral phases) found by SAES significantly exceeds the list of minerals found previously by SEM–EPMA because of different natures of optical and X-ray spectra. The sizes of PM particles calculated by the SAES method and measured by SEM–EPMA are similar. The SAES data on the total concentrations of PMs satisfactorily agree with the results of inductively coupled plasma mass spectrometry.

Keywords: gold, silver, platinum, palladium, iridium, osmium, rhodium, ruthenium, electron probe microanalysis, scintillation atomic emission spectrometry, geological samples, Natalka, Pavlik, Vetrenskoe, and Degdekan gold ore deposits

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The data on mineral phases (species) of PMs and sizes of their particles in rocks, ores, and technological ore processing products are of paramount importance even if the total concentrations of precious metals slightly exceed average abundance in the Earth's crust, because they allow the determination of mineral paragenesis accompanying ore mineralization processes and their use for the predictive assessment and revelation of ore bodies and the development and adaptation of separate steps of enrichment technologies in the variation of the composition of the initial ores for increasing the recovery of useful components [1–3].

In the last decades, in the study of platinum mineralization accompanying gold deposits, researchers widely used electron probe microanalysis, combining scanning electron microscopy and electron probe X-ray microanalysis, SEM–EPMA [4], for the determination of the elemental composition of substances in small volumes; for the search for and determination of the elemental composition of rare minerals found in trace amounts; and also for the assessment of their linear sizes. Difficulties in the application of the specified method to the search for minerals concentrating gold, silver, and platinum-group metals (PGMs: Pt, Pd, Os, Ir, Rh, and Ru) are associated with their low total concentrations and the nonuniform distribution of mineral phases in geological samples. In this connection, rock-forming and ore minerals are usually preseparated (by gravimetric preconcentration, separation, flotation, etc.), because of which the required mineral phases carrying PMs may be quite often lost. Big errors in the determination of elemental compositions by EPMA (up to 100%) can be associated with the microrelief of the sample surface [5].

The qualitative and quantitative problems of mineralogical analysis in the search for rare mineral PM phases are also successfully solved by scintillation atomic emission spectrometry with arc discharge (SAES) [6–10]. The SAES method allows the determination of total concentrations of precious metals in powdered bulk samples without the preliminary separation of the ore and accompanying minerals; the elemental composition of particles carrying PMs; and also the assessment of the sizes of these particles and their size distribution. The instrumentation of SAES is intensively developed [11, 12], analytical procedures are improved, and the limits of detection for gold, platinum, and palladium are lowered [10]. The SAES methodology, including the conditions of the emission and recording of spectra, calibration of the spectrometer by the wavelength, and the assessment of the effect of spectral overlaps, calculations of zero thresholds and particle sizes, procedures for counting particles in the required size ranges, calibration by standard samples for the determination of total concentrations of PMs, and the assessment of the elemental compositions of individual particles of each mineral phase was described in detail in [6–10].

SAES and SEM–EPMA were used for the determination of precious metals in geological samples from four gold ore deposits in the North-East of Russia: Natalka, Pavlik, Vetrenskoe, and Degdekan.

EXPERIMENTAL

Samples from gold deposits Natalka (N-11-1-19), Pavlik (P-11-2-4 and P-11-2-9) and Degdekan (Dn-22) presented by silicate rocks (aleurolites with inclusions of a tuffaceous impurity no more than 5%, fine quartz veinlets and sulfide impregnations of about 3%) from ore deposits, and clay shales from the ore pit of the Vetrensky deposit (V-11-2-8 and V-11-2-4) containing sulfide impregnations of no more than 1% were studied by SAES and SEM–EPMA.

Representative parts of samples for the used analytical methods, except for SEM–EPMA, were crushed to particle size less than 0.08 mm. Total concentrations of PMs, except for osmium, were determined by inductively coupled plasma mass spectrometry (ICP MS) from weighed portions of 2 g. Powders of the above samples were analyzed by SAES on two instrumental complexes from VMK-Optoelektronika Ltd. (Russia). Complex 1 [10] works in the Vinogradov Institute of Geochemistry SB RAS (Irkutsk) and complex 2 [11, 12], in the Institute of Automation and Electrometry SB RAS (Novosibirsk). The specific features of the instrumental complexes and the operation conditions of analysis are summarized in Table 1. Samples with high concentrations of PMs before analysis were diluted with a neutral medium, a "blank" sample or a graphite powder (1 : 3, 1 : 10), because the upper boundaries of the analytical ranges for PMs do not exceed 10–15 mg/kg. The coefficient of efficiency of the powders in the injection–spilling way is usually 15–30%; therefore, the recorded analytical signals incompletely characterized masses of the initial samples. Counting of the number of particles of rare mineral PM phases present in the sample and the determination of their elemental composition (mineral phases) were performed using the Correlation Analysis module incorporated in the "Atom" software (Fig. 1). The operation algorithm of the module consisted in the approximation of the spectral background in the vicinity of the analytical line, minimization of background fluctuations, and the construction of a time dependence of the intensity of the spectral line of an analyte followed by the extraction of single or group scintillation signals. The spectral background in the vicinity of the analytical line was approximated in three dimensions (wavelength, intensity, and time) by a function specified as a product matrix of two vectors, $\overline{B} = \overline{V_\lambda} \times \overline{V_t}$, where $\overline{V_\lambda}$ is the vector approximating the background along wavelengths in the vicinity of the analytical line, $\overline{V_t}$ is the vector describing background fluctuations with time. The minimization of background fluctuations was done using the "Atom" software according to the algorithm proposed in [13]. Then the set of recorded scintillations from the specified spectral lines was separated into non-overlapping sets of single and simultaneous (group) flashes. The advantages of complex 2 were in a higher resolution and an improved signal-to-noise ratio, which ensured the reliable separation of peaks of closely lying spectral lines of elements and a possibility of recording spectra of not only Au, Ag, and six PGMs, but also of seven elements (Fe, S, As, Sb, Se, Te, W) forming widespread mineral phases containing PMs [14–16] in the scintillation mode. The limits of detection for total concentrations of elements by the SAES method for complexes 1 and 2 were estimated on the same sets of standard samples. They were as follows, mg/kg: Au 0.004; Ag 0.05; Pt 0.03; Pd 0.0013 [8]; and Rh, Ru, Ir, and Os, no more than 0.005. The limits of detection for the other elements by atomic emission spectrometry with the introduction of powdered samples into the arc discharge by injection–spilling way and integrated registration of spectra were in the region 0.0001–0.005 wt % [17] and were lowered by 1–2 orders of magnitude in the scintillation recording of spectra [18]. The spectral lines of Se and S were recorded in the scintillation mode at concentrations ~5 wt %. This was sufficient for the determination of the macroelemental composition of PM minerals, because the concentrations of sulfur and selenium in PM sulfides and selenides were usually higher than 10–20 wt %. To assess the particle size of PM carriers by SAES, we used experimentally found exponential and power dependences, relating the intensity of the scintillation of native metal particles with the diameter of particles in five intervals: 2–6, 6–10, 10–16, 16–22 and > 22 μm [8]. Complex 1 provided the reliable registration of scintillation signals from PM species with diameters more than 2 μm [8, 19]. The upper boundary of the fifth range was not normalized because the powders were comminuted to particle size less than 80 μm. For complex 1, the consecutive description of the procedure for the implementation of scintillation arc atomic emission analysis, methods of searching for and processing of analytical signals for the calculation

Table 1. Operation conditions of the determination of precious metals by SAES [8, 13]

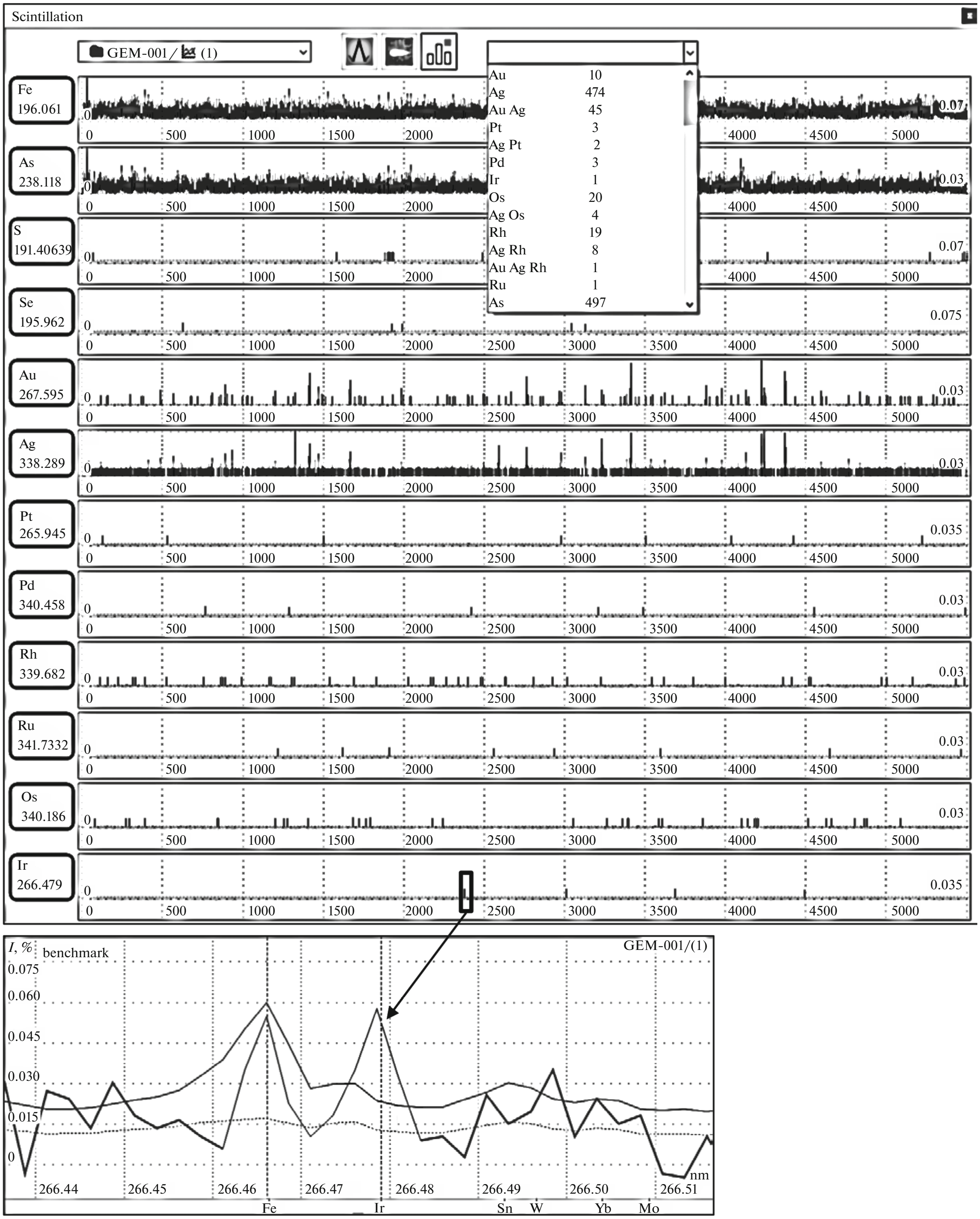
Conditions of spectrum excitation, recording and processing	Complex 1	Complex 2
Introduction of powdered samples into the arc discharge	“Potok” installation, injection–spilling way	
Spectral analytical generator	“Fireball”	
Alternating current, A	20–22	
Weighed portion, mg	150	
Powder delivery rate, mg/s	8–9	
Total exposure, s	17	
Spectrometer	STE-1	Grand-1500
Spectrometer slit illumination system	Three-lens	Two-lens
Photodiode arrays	BLPP-369M4	BLPP-2000
Number of arrays	4	
Basic exposure, ms	4	3
Resolution, pm	9–15	6–7
Elements whose atomic emission spectra are recorded in the scintillation mode	4 elements: Au, Ag, Pt, Pd	15 elements: Au, Ag, Pt, Pd, Ir, Os, Rh, Ru, Fe, S, As, Sb, Se, Te, W
Spectrum processing software	“Atom” software with “Correlation Analysis” module; MS Excel	

of total concentrations of PMs, the determination of the chemical composition of individual particles carrying PMs, and the assessment of their sizes were presented in [10, 19]. The methodology of analysis using complex 2 was similar.

The search for and analysis of rare mineral phases of precious metals by SEM–EPMA were performed using the instrumental–software QEMSCAN (FEI, Netherlands) installed in the Shilo North-East Interdisciplinary Research Institute, Far East Branch, Russian Academy of Sciences (Magadan). The complex represented an EVO-50 scanning electron microscope (Carl Zeiss, Germany) equipped with four energy-dispersive (EDS) AXS XFlash spectrometers (Bruker, Germany), a Quantax Esprite system of X-ray microanalysis, and special software ensuring the automation of the analysis of the mineral composition of geological samples. The QEMSCAN involved the instrument–software synchronization of the data obtained from the back scattered electron detector (BSE detector) and EDS detectors arranged according to the scheme “one opposite another,” which allowed us to analyze unpolished samples. The company developed the QEMSCAN proposed a number of special procedures for sample preparation and developed corresponding equipment used in [20–22]. Samples were crushed to fineness less than 160 μm and a heavy fraction was extracted with tribromomethane from a weighed portion of 0.65 g using the procedure proposed by the manufacturing company. Substance of the heavy fraction (minerals and their intergrowths with silicates) of the size <1–25 μm was applied as a thin layer onto a conducting carbon adhesive tape and carbon was sputtered. The conditions of measurements were as follows: accelerating voltage 25 kV, beam current 120 pA (QUANTAX mode) or 5 nA (QEMSCAN mode), size of emitting area 4 μm. The search for and study of mineral phases were performed in the BSE mode. The quantitative analysis of grains (mineral phase) was performed using the QUANTAX software and the so-called standardless P/B-ZAF method. Minerals were searched for visually at the image-by-image area scanning. Linear sizes of mineral phases revealed by brightness were measured and their elemental compositions were calculated by the total spectrum. Mineralogical analysis by SEM–EPMA was conducted for all of the above samples to describe the total mineral composition and all PM species present. The results included data acquisition for mineral phases of gold, silver, and PGMs; the assessment of the size distribution of gold particles and of the degree of gold release [20, 22].

RESULTS AND DISCUSSION

The results of analysis of samples from four deposits by SAES are presented in Tables 2–4, including data on the number of particles carrying each precious metal and the found total concentrations of Au, Ag, Pt, and Pd. Despite the analysis of unrepresentative portions, in samples we found and identified particles containing all PMs, including extremely rare Ir, Ru, Pt, and Os. The errors of the determination of the total concentrations of PMs depended on concentrations and varied from 3–10 to 3–50 rel. % in different samples. The results were verified by the analysis of stan-



Au	10
Ag	474
Au Ag	45
Pt	3
Ag Pt	2
Pd	3
Ir	1
Os	20
Ag Os	4
Rh	19
Ag Rh	8
Au Ag Rh	1
Ru	1
As	497

Fig. 1. Fragment of work of the "Correlation Analysis" module of the "Atom" software. Time dependence of the intensity of individual flashes from the substance of a sample of the Natalka deposit. Scintillation spectra at the wavelengths of analytical lines of Fe, As, S, Se, Au, Ag, Pt, Pd, Rh, Ru, Os, and Ir; results of counting the number of particles of the specified composition. A fragment of scintillation spectrum in the 7.122th s in the vicinity of analytical lines of iron and iridium.

Table 2. Number of particles carrying precious metals detected by SAES and total concentrations of precious metals in N-11-1-19 sample from the Natalka deposit ($n = 5$, $P = 0.95$)

Element	Amount of PM-containing particles in the sample			Total concentration, mg/kg		
	particles of native PM; PM with an admixture of iron; intermetallides and solid solutions of PM, possible halides	PM particles of complex composition (arsenides, sulfides, sulfoarsenides, sulfosalts, antimonides, tellurides, and selenides)	totally	SAES		ICP MS
	Complex 2				Complex 1	
Au	177	30	209	1.1	9.4	0.981
Ag	1510	875	2385	0.37	0.53	0.42
Ir	13	2	15	no define		
Os	57	22	79			
Pd	86	215	301	no define	0.0047	0.0045
Pt	32	11	43		<0.03	0.102
Rh	68	14	82		<0.005	0.00018
Ru	12	21	33		<0.005	0.00045

dard samples of the composition of black shales SChS-1 and SLg-1 [8, 19]. A comparison of total concentrations found by SAES with the results of ICP MS analysis indicated the greatest differences in the determination of gold. The results of gold determination by SAES in two samples from the Pavlik deposit appeared 10 times lower and in the Natalka and Vetrenskoe samples, higher than the data of ICP MS. However, the results of determination of the total concentrations of gold by SAES and atomic absorption spectrometry [23] agreed well: the coefficients of correlation were 0.9 and 0.8 (Table 5). It was also shown that, with an increase in the total concentration of gold, the number of larger Au particles grew, changing their size distribution. The results of the determination of silver by SAES and ICP MS well agreed for all samples except for Dn-22 (Degdekan deposit). The concentrations of platinum and palladium significantly differed only for samples from the Pavlik deposit. Taking into account that the determination of total concentrations by SAES was done for analytical weighed portions smaller than those used in ICP MS, the results of PM determination can be recognized comparable.

Natalka deposit. In the processing of five scintillation spectra of N-11-1-19 sample (mass of initial sample 0.75 g), we found particles carrying PMs of various compositions, which were described by both mono- and multielement (up to six elements) associations (Table 2). Figure 1 presents an example of work of the "Correlation Analysis" module in estimating the composition of particles of the specified element associations and counting their numbers in a spectrum of N-11-1-19 sample, GEM-001. More than 2000 monoelement particles were assigned to native gold (30 particles) and silver (more than 900 particles), six PGMs, tungsten and iron, and also to PM intermetallides with metals; not detected in the scintillation mode (Ni, Cu, Bi, Pb, etc.) and, probably, to PM halides. We found particles of electrum (Au–Ag, 97), acanthite Ag_2S (Ag–S, 21), and hessite Ag_2Te (Ag–Te, 4) and dozens of particles of the compositions Pd–Ag (46), Pd–Fe (13), Rh–Fe (10), Au–Fe (11), Au–Ag–Fe (33), Pd–Ag–Fe (20), Pd–As (14), Rh–As (11), Ag–As (>360), Au–Pd–As (17), Au–Ag–As (37), Pd–S (11), and Ag–Sb (11). Mineral phases of the following composition were found: Au–Pt (1), Ir–Ag (1), Pd–Pt (1), Pt–Ag (2), Os–Ag (3), Ir–Fe (5), Os–Fe (6), Pt–Fe (2), Ru–Fe (3), Au–Ag–Os (2), Os–Ag–Fe (2), Rh–Ag–Fe (5), Au–As (7), Os–As (7), Pt–As (4), Au–S (6), Au–Ag–S (6) Pd–Ag–S (4), Pd–Sb (2) Pd–Sb–S (3), Pt–Sb–S (5), etc. For more than 40 particles found by SAES, composition was described by the element association Sb–S; they were considered as mineral phases of antimonite (Sb_2S_3), tetrahedrite (Cu_3SbS_3), and boulangerite ($Pb_5Sb_4S_{11}$), accompanying the mineralization of gold [22, 24]. The same papers reported about the detection of native gold, silver, and cadmium and electrum, acanthite, and hessite by the EPMA; however, native PGMs have not been found previously.

In samples **from Pavlik and Vetrenskoe deposits** (Table 3), particle detected by SAES were divided into compound classes taking into account previously published data on the found minerals [20–22, 24–26] and specific physical and chemical features of elemental compositions of natural phases containing PMs [14, 15]. Monoelement particles were assigned to class 1. Such scintillation signals were obtained from particles of native PMs, probably, PM halides, and minerals

Table 3. Number of particles carrying precious metals detected by SAES and total concentrations of gold, silver, and platinum-group metals in samples from Pavlik and Vetrenskoe deposits ($n = 4–6$, $P = 0.95$)

Deposit name and sample weight	PM	Amount of PM-containing particles in the sample							Total concentration, mg/kg		
		compound class						totally	SAES		ICP MS
		1	2	3	4	5	6		complex 2	complex 1	
		SAES – complex 2									
Pavlik P-11-2-4 (IS* 0.75 g)	Au	39	33	17	94	1	–**	184	0.033	0.025	0.307
	Ag	928	716	152	2586	20	3	4405	0.66	0.46	0.37
	Pd	8	8	10	38	2	–	66	not detected***	0.0043	0.00217
	Pt	35	3	–	21	1	–	60		<0.03	0.00075
	Ir	–	–	–	–	–	–	–		not detected	not found ****
	Os	28	16	–	30	–	–	74			not detected
	Rh	54	22	–	21	–	–	97		<0.005	not found
	Ru	11	–	–	1	–	–	12		<0.005	not found
Pavlik P-11-2-9 (IS 0.6 g)	Au	262	318	16	631	7	6	1240	0.16	0.039	1.28
	Ag	1988	1231	51	3357	37	21	6685	2.1	2.2	2.37
	Pd	107	60	6	85	2	1	261	not detected	0.004	not detected
	Pt	20	19	1	13	–	–	53		0.43	0.003
	Ir	–	1	–	–	–	–	1		not detected	not found
	Os	41	22	–	28	–	–	91			not found
	Rh	37	21	–	16	–	–	74		<0.005	not found
	Ru	4	2	–	1	–	–	7		<0.005	0.0001
Vetrenskoe V-11-1-8 (IS 0.6 g)	Au	410	1198	114	1050	1240	94	4106	5.6	17	2.31
	Ag	687	1451	158	1829	1322	134	5581	0.75	0.81	0.23
	Pd	85	52	17	67	45	9	275	not detected	<0.0015	0.00002
	Pt	30	18	–	28	26	1	103		0.05	0.00007
	Ir	16	12	–	12	10	–	50		not detected	0.00045
	Os	25	28	3	22	19	4	101			not detected
	Rh	48	36	6	30	14	2	136		<0.005	0.00023
	Ru	5	2	3	3	3	3	19		<0.005	0.0004
Vetrenskoe V-11-2-4 (IS 0.96 g)	Au	875	2690	9	1058	1962	20	6614	37.5	40	58.8
	Ag	2204	3317	13	2124	2075	27	9760	1.55	2.35	2.1
	Pd	119	97	1	62	111	1	391	not detected	<0.0015	0.00213
	Pt	11	12	–	8	13	1	45		<0.03	0.00237
	Ir	20	13	–	3	2	–	38		not detected	0.00013
	Os	79	62	–	25	21	–	187			not detected
	Rh	110	75	2	41	21	–	249		<0.005	0.00017
	Ru	21	11	–	9	10	–	51		<0.005	0.00027

* IS is total sample weight for which particles were counted.

** Particles were not found.

*** The total concentration of PM was not determined.

**** The element is not found by ICP MS (element is lower than the limit of detection of the procedure).

Table 4. Number of the particles containing precious metals and total concentrations of precious metals in sample from the Degdekan deposit ($n = 3$, $P = 0.95$)

PM	Amount of PM particles in the initial sample Dn-22							Total concentration, mg/kg	
	particles of native PM; PM intermetallides with an admixture of iron, and PM halides	particles of complex composition, including PM and the above elements					amount of particles containing each PM	SAES (complex 1)	ICP MS
		S	Sb	As	Te	Se			
	SAES (complex 2)								
Au	94	1	–*	24	6	1	126	0.29	0.235
Ag	2490	51	23	568	45	5	3182	0.89	4.28
Ir	3	–	–	–	–	–	3	no define	0.00052
Os	42	–	1	9	3	–	55		no define
Pd	95	3	3	21	10	1	133	<0.002	0.00152
Pt	11	–	–	2	–	–	13	<0.03	0.00562
Rh	38	–	–	2	–	–	40	<0.005	0.00014
Ru	6	–	1	3	2	–	12	<0.005	0.00061

* Particles of the specified composition were not found.

Table 5. Determination of total concentrations of gold and the size distribution of gold particles (SAES, complex 1) in selected samples from Natalka and Degdekan deposits ($n = 2$–4, $P = 0.95$)

Deposit	Sample set	Particle distribution by diameter (μm), in % to the amount of detected gold particles					Total concentration of Au, mg/kg		Correlation coefficient
		2–6	6–10	10–16	16–22	>22	SAES	AAS*	
Natalka	10	100	–**	–	–	–	<0.01	0.006	0.90
	8	99–68	1–32	–	–	–	0.18	0.147	
	8	75–48	8–43	0–10	0–6	0–25	0.67	0.54	
	7	66–26	20–45	2–7	2–8	4–23	2.6	2.08	
Degdekan	22	100	–	–	–	–	0.017	0.013	0.83
	14	94–60	6–40	–	–	–	0.045	0.036	
	5	83–50	0–31	8–25	–	–	0.18	0.11	
	8	94–50	5–40	0–10	0–10	0–11	0.41	0.27	
	16	59–24	24–47	1–22	1–10	0–18	2.04	1.98	

* AAS is atomic absorption spectrometry with the extraction of gold into oil sulfides, performed in the Vinogradov Institute of Geochemistry of the Siberian Branch of the Russian Academy of Science using procedure [23].

** No particles with linear dimensions in the specified range.

containing individual PMs and one or several metals (Me = Pb, Cu, Zn, Ni, Co, Mo, Sn, Bi, Cd, etc.), which form mineral phases with PMs, but were not recorded in the scintillation mode because of technical limitations: PM, PM (Me), and PM (halogen). Class 2 was formed by solid solutions of PMs with each other and with an admixture of iron and other metals: PM–PM; PM–PM(Me); PM–PM–Fe(Me). Class 3 particles were PM compounds with sulfur: PM–S; PM–P(Fe)–S; PM–P(Fe)–Me–S. Class 4 consisted of compounds of individual PMs formed between different PMs and with other metals, including arsenic, antimony, and sulfur individually or in different combinations: PM–As(Sb, S); PM–PM(Fe)–As(Sb, S); PM–PM–PM(Fe)–As(Sb, S). Class 5 was formed by compounds of one or several PMs with tellurium, arsenic, antimony, and sulfur: PM–Te, PM(Fe)–Te, PM–As(Sb, S), and PM–PM(Fe)–Te–As(Sb, S). Class 6 particles were selenides of individual PMs or their combinations with As, S, and Sb impurities:

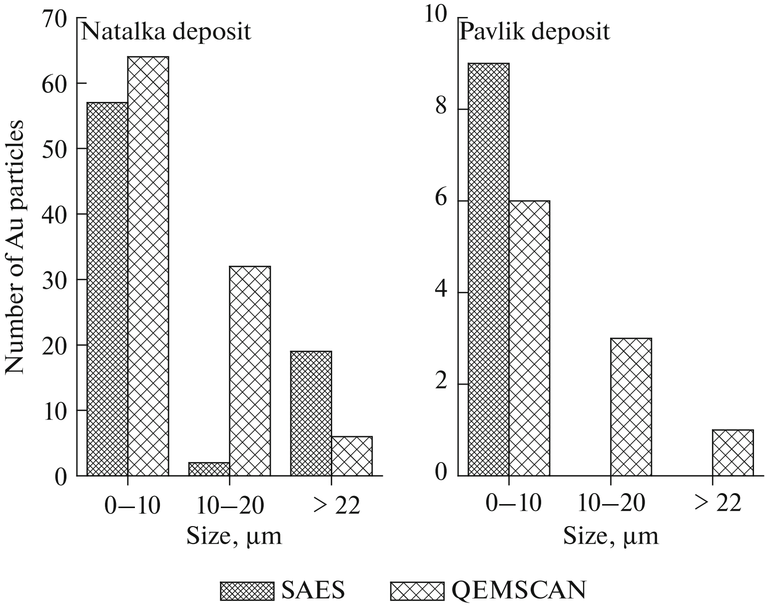


Fig. 2. Size distribution of gold particles in the initial samples according to SAES; SEM–EPMA (QEMSCAN) in concentrates.

PM–Se, PM–PM–Se, PM–As–Se, PM–PM–As–Se, PM–As–Sb–Se, PM–As–S–Se, and PM–As–Sb–Se.

Similar compound classes present in black shales were reported in the paper by Laverov with coauthors [1]. The subdivision of element associations found by SAES into the above classes, we used for the presentation of PM-carrying particles in samples from Pavlik and Vetrenskoe deposits (Table 3), agrees with mineral classifications by Vernadsky and Kostov [27], which allowed us to reveal the elemental compositions of particles carrying PMs characteristic for each deposit. In samples from the Pavlik deposit, the greatest number of particles carrying PMs corresponded to elemental compositions characterized by classes 1, 2, and 4 (Table 3). Particles containing iridium and ruthenium were not present or were very few in all classes, except for the first one (these were, probably, native metals). Numbers of particles containing Pd, Os, Rh, and even Pt were dozens and those containing Au, hundreds. An increase in the total concentration of gold and silver was characterized by the appearance of their selenide species. Another pattern was observed for samples from the Vetrenskoe deposit. The total (over all classes) number of particles carrying Ir, Ru, and Pt was several dozens; Pd, Os, and Rh, hundreds; and of Au and Ag, thousands. The maximum number of mineral phases of PMs was presented not only by metals and intermetallides of classes 1 and 2, but also by compounds with tellurium, arsenic, and antimony of compound classes 5 and 4. In samples from the Vetrenskoe deposit, in comparison with those from the Pavlik deposit, the number of gold and silver selenide particles increased and PGM selenides, except for Ir, were observed (Table 3, class 6).

The sizes of particles containing Au, Ag, Pt and Pd in samples from Natalka, Pavlik, and Vetrenskoe deposits are presented in Table 6 according to the data of SAES and SEM–EPMA. Particle sizes of native metals and solid solutions Au–Ag calculated by the SAES method appeared to be ≤2–5 μm, rarely 5–10 μm or more, which well agrees with the data of SEM–EPMA. However, the number of the found phases appeared much more. Dozens of Pt and Pd particles were found and identified in the initial powders only by SAES. These mineral phases were, probably, not present in the heavy concentrates prepared from the initial powdered samples for the QEMSCAN complex. The size distributions of Au particles (Fig. 2) obtained according to SAES and SEM–EPMA data for samples from Natalka and Pavlik deposits significantly differed for the same reasons.

The **Degdekan** gold ore **deposit**, like the Natalka and Pavlik deposits, is located in black shale complexes of the Verkhoyansk–Kolyma folded region [20, 25, 26, 28]. Samples selected in different areas of the ore deposit were similar in the concentrations of chemical elements and composition of mineral associations [28]; therefore, the results of analysis of a Dn-22 sample by SAES (Tables 4 and 7) were compared with the data of SEM–EPMA also obtained for other samples from this deposit. In the analysis of the material of the initial Dn-22 sample from the Degdekan deposit, weighing about 2 kg, by SEM–EPMA, 23 particles of mineral phases containing Os, Ir, and Ru were found in the prepared concentrate [20]. Minerals containing Pt and Pd could not be found, in spite

Table 6. Some element associations, amount, and size of particles detected by SAES; mineral phases, amount of their particles, and size found by SEM–EPMA in samples from different deposits

Sample	SAES			SEM-EPMA		
	element association	particle amount	size, μm	particle amount	size, μm	mineral, formula
Natalka						
N-11-1-19	Au	30	<2...>30	102	<2...10, rarely 30–40	Native Au
	Ag	>900	<2...20	–*	–	–
	Au–Ag	97	<2...10	41	1...3, more rarely 8–15	Solid solution Au–Ag
	Au–Te	4	<2...10	1	8	Hessite Ag_2Te
	Pt	24	<2...5	–	–	–
	Pd	4	<2...3	–	–	–
Pavlik						
P-11-2-4	Au	39	<2...6	–	–	–
	Ag	>600	<2...10	3	From 1.1 to 5.0	Native Ag
	Au–Ag	10	<2...10	–	–	–
	Ag–Se	1	5	1	1.5	Naumannite Ag_2Se
	Ag–Au–Se	–	–	13	0.6–2.5	Fishesserite Ag_3AuSe_2
	Pt	8	<2...3	–	–	–
	Pd	24	<2...3	–	–	–
P-11-2-9	Au	69	<2...6	10	10, more rarely 20–30	Native Au
	Ag	>1000	<2...10, rarely 15	2	1.1 and 1. 5	Native Ag
	Au–Ag	180	<2...10, rarely >20	1	1.0	Solid solution Au–Ag
	Ag–Se	11	–	–	–	–
	Ag–Au–Se	3	–	14	0.4–1.2	Fishesserite Ag_3AuSe_2
	Pt	20	<2...3	–	–	–
	Pd	94	<2...3	–	–	–
Vetrenskoe						
V-11-1-8	Au	>200	Homogenous from <2 to 20 and rarely larger	10	0.8–2.4, more rarely to 20	Native Au
	Ag	>400	Often 6–10, rarely to 20 and larger	–	–	–
	Au–Ag	>400	<2...10, rarely 20	38	0.6–4.0; rarely 10–30	Solid solution Au–Ag
	Ag–Au–Se	18	–	4	1–1.5	Fishesserite Ag_3AuSe_2
	Pt	30	<2 to 10	–	–	–
	Pd	74	<2...3	–	–	–
V-11-2-4	Au	>300	<2 to 25	–	–	–
	Ag	>500	Mainly 6–10, rarely to 20 and larger	–	–	–
	Au–Ag	>500	–	100	From 10 to 147	Solid solution Au–Ag
	Ag–Au–Se	3	–	–	–	–
	Pt	10	<2 to 10	–	–	–
	Pd	71	<2...3	–	–	–

* Particle of the specified composition is not found, size is not found, mineral phase is not determined.

Table 7. Amount of particles (*N*) of some element associations of precious metals detected in a sample of the Degdekan deposit

Element association	*N*	Element association	*N*	Element association	*N*
Au*	17	Pt–Ag–Fe	2	Pd–Fe–As	6
Ag	1230	Rh–Ag–Fe	7	Rh–Fe–As	1
Os	16	Ru–Ag–Fe	1	Au–Ag–Fe–As	9
Pd	57	**Ag–S**	20	Os–Ag–Fe–As	2
Pt	5	Au–S	1	Au–Os–Fe–As	1
Rh	20	Pd–S	1	Pd–Ag–Fe–As	4
Ru	3	Pd–Ag–S	1	Rh–Ag–Fe–As	1
Au–Ag	40	Ag–Fe–S	30	Ag–Au–Ru–Fe–As	1
Os–Ag	9	Pd–Fe–S	1	Ag–Fe–As–S	6
Pd–Ag	9	**Ag–Se**	3	Ag–Fe–Sb–As	2
Pt–Ag	3	**Ag–Au–Se**	1	**Ag–Sb**	4
Rh–Ag	9	Ag–As	234	Pd–Sb	1
Au–Pd–Ag	2	Au–As	1	Ru–Sb	1
Ag–Fe	1130	Os–As	3	Ag–As–S	2
Au–Fe	8	Pd–As	9	Ag–Sb–As	3
Ir–Fe	3	Pt–As	2	Ag–Fe–Sb	17
Os–Fe	11	Au–Ag–As	11	Pd–Te	1
Pd–Fe	12	Au–Ru–As	1	Os–Te	1
Pt–Fe	1	Pd–Ag–As	2	**Ag–Te**	10
Rh–Fe	2	Ru–Ag–As	1	Ag–Fe–Te	9
Au–Ag–Fe	25	Os–Ag–As	2	Au–Pd–Te–As	2
Os–Ag–Fe	4	**Ag–Fe–As**	300	Au–Os–Pd–Ru–Ag–Te–As	2
Pd–Ag–Fe	15	Os–Fe–As	1	Ag–Fe–Te–As	4

* Element associations corresponding to all PM mineral phases [20, 22, 28, 29] found previously by EPMA are given boldface.

of the fact that their total concentrations were earlier quantitatively determined by various analytical methods [21]. A study of samples from this deposit [28] also did not result in the detection of mineral phases of Pt and Pd by SEM–EPMA because of insufficient limits of detection for Pt and Pd, though in the light, sulfide, and electromagnetic fractions extracted from these samples, the variations of total concentrations were as follows, mg/kg: Pt 0.01–3.42 and Pd 0.07–0.25.

Using the SAES method, in the powder of the initial Dn-22 sample, we detected and identified mineral phases containing both individual particles of gold, silver, all six PGMs, and particles of complex elemental composition (Table 4). Most particles were presented by metals and intermetallides, probably, PM halides, particles of complex compounds were mainly PM arsenides. The compositions of some particles of the initial Dn-22 sample and their numbers found by SAES method are presented in Table 7. Compounds whose elemental compositions corresponded to accompanying minerals found previously by SEM–EPMA, i.e., pyrite, arsenopyrite, antimonous pyrite and arsenopyrite, scorodite and their intergrowths with Ag, Au, and PGMs, electrum and kustelite, native antimony, antimonite, acanthite, pearceite, dyscrasite, polybasite, etc. [20, 26, 28, 29] are given boldface. Dozens of particles containing Pt and Pd were found in the samples only by SAES, the use of which ensured the assessment of not only their sizes, but also total concentrations satisfactorily agreed with data of ICP MS (Table 4).

In the powder of the initial Dn-22 sample, the sizes of numerous particles of native gold, silver, and their solid solutions varied from ≤2 to 10–15 and more μm according to SAES data; the sizes of native particles, intermetallide particles, or particles of Os, Pd, Rh, and Ru halides were smaller than 2 μm; and those of Pt, up to 6 μm. According to SEM–EPMA, particle sizes in the concentrates were <2 μm for Au and Ag (native) [20, 28]; up to 5 μm for Au–Ag intermetallides [28]; and from 0.5 to 5 μm for native osmium, Ru–Ir–Os minerals, and their arsenide [20]. The sizes of particles carrying PMs found by SAES and SEM–EPMA in a sample from the Degdekan deposit were close to each other, which was also shown for gold particles from the Sukhoi Log deposit (Russia, Irkutsk region) [19].

Differences in the amounts and elemental compositions of particles carrying PMs found by SAES and EPMA can be explained by lower limits of detection in atomic emission spectrometry and no losses of individual mineral phases (in particular, small and light) from the powder of the initial sample in the extraction of heavy fraction concentrates.

* * *

Therefore, in the study of substances from Natalka, Pavlik, Vetrenskoe, and Degdekan (North-East of Russia) gold deposits by the SAES method, in each sample we found dozens and hundreds of particles carrying PMs, including native metals, intermetallides, and solid solutions, arsenides, antimonites, sulfoarsenides, tellurides, selenides, etc. The number and variety of the found element associations (compounds) containing PMs significantly exceeds the list of their minerals found by the SEM–EPMA method. Each deposit is characterized by an individual set of element associations (mineral phases), which probably depends on the features of the ore formation processes. The amount of particles detected by SAES reflects the ratio of average abundance of PMs in the Earth's crust. The calculated particles sizes found by SAES well agree with SEM–EPMA estimates. A comparison of the results obtained by SAES and EPMA showed that the data on the same gold-bearing sample can significantly differ. The reason may be the difference in the limits of detection by these methods by several orders of magnitude because of different natures of optical and X-ray spectra. Note that SEAS is used to analyze powders of the initial sample, and EPMA, only concentrates of mineral phases extracted from this powder according to certain procedures. These features of methods must be taken into account in the interpretation of the results of analysis. The wide acceptance of the SAES method for simultaneously gaining information about the elemental and material composition of samples in the study of gold ore deposits requires the further improvement of the spectral equipment and software.

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