

Modes of Au, Pt, and Pd Occurrence in Arsenopyrite from the Natalkinskoe Deposit, NE Russia

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Abstract—Pioneering data obtained by studying arsenopyrite from the Natalkinskoe deposit indicate that the mineral contains equidistributed Au, Pt, and Pd in two major non-mineral modes: structural and surface-bound. High Au, Pt, and Pd concentrations in the arsenopyrite are proved to be related to the surface-bound mode. No individual Pt and Pd minerals were detected, while Au occurs mostly in the form of native metal. Variably sized native Au grains (mostly small ones) form aggregates with arsenopyrite and quartz and occur in them as small inclusions. The situation with Pt and Pd is different: arsenopyrite is likely the main concentrator of the elements. Gold-bearing arsenopyrite seems to accommodate all admixtures according to a single mechanism, in which an active role is played by the surface of crystals of the mineral and its surface defects. In view of this, it is possible to recover refractory gold without disintegrating the structure of the mineral, a fact that should be taken into account at, for example, processing ores containing sulfides, for instance, arsenopyrite.

Keywords: gold deposit, arsenopyrite, gold, platinum, palladium, modes of occurrence

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INTRODUCTION

Studying mineral and non-mineral modes in which ore elements occur to get insight into the genesis of mineral deposits is one of the top-priority tasks of the geochemistry of ore-forming processes. Along with mineral and micromineral modes, much research is currently centered on the problem of so-called “invisible” modes in which elements may be contained in ore minerals. When studying gold deposits, both national and foreign geologists traditionally focused attention mostly on finely divided “invisible” gold in sulfide minerals, first of all, in pyrite (Kravtsova and Solomonova, 1984; Kravtsova, 1985, 2010; Kravtsova and Andrulaitis, 1989; Cook and Chrystoulis, 1990; Genkin, 1998; Tauson and Kravtsova, 2002, 2004; Palenik et al., 2004; Reich, 2005; Tauson et al., 2008, 2009, 2014; and others). This “invisible”, or so-called refractory, gold occurs in ores of various types and is refractory to conventional processing by means of cyanide leaching. It is now particularly important to study this problem because of rising gold prices. Much attention is currently paid to quantitative assessments. For example, it was demonstrated at mineral deposits of various genesis, which host ore mineralization of various types, in northeastern Russia (Dukat, Dal’nee, Oroch, Natalkinskoe, and Degdekan), Amur area (Pokrovskoe), eastern Siberia (Sukhoi Log), eastern

Transbaikalia (Amurskie daiki and Novinka), the Eastern Sayan (Zun-Kholba), and the western Tien Shan (Kochbulak and Kyzylmasai) that equidistributed “invisible” gold is contained in pyrite in two modes: structural and surface-bound. The latter is related to nanometer-sized nonautonomous phases on the surface of pyrite crystals and is fairly often dominant (Tauson and Kravtsova, 2002, 2004; Tauson et al., 2009, 2014). Micro- and nanometer-sized particles of elementary Au (Au⁰) can be formed when these phases are modified after their growth (Tauson et al., 2014).

We have remarkably widened the circle of studied ore minerals and elements. Among sulfides, these are (in addition to pyrite) galena (from the Zun-Kholba deposit) and arsenopyrite (Amurskie Daiki), although both minerals are still examined not very thoroughly. The only studied oxide is magnetite (from the Novinka deposit). The very first data are obtained on the distribution and modes of occurrence in pyrite of such Au-accompanying elements as Ag, Sb, As, Bi, Cu, Mn, Ni, and B. Even the first scarce data led us to suggest that the dependence of the content of equidistributed gold on the size of its particles and the relation of much of this gold to the surfaces of crystals is a feature shared by all ore minerals, whereas the structural and surface-bound modes, which are dominant for equidistributed

gold, may also be typical of other ore elements (Tauson et al., 2014).

The data thus obtained demonstrate that this avenue of studying ore minerals on a nanometer scale is highly promising in both its theoretical and applied aspects and should be continued. Our earlier studies were continued, and below we present data on the modes of Au, Pt, and Pd occurrence in arsenopyrite at the Natalkinskoe gold deposit in northeastern Russia. Our analyses for structural and surface-bound Au in arsenopyrite from the deposit and data on Pt and Pd are pioneering. It should be stressed that we have not detected any individual Pt and Pd minerals in the ores of the deposit, in spite of the fact that these ores persistently contain 0.1–0.2 ppm of both metals.

MATERIALS

The Natalkinskoe gold deposit of Late Paleozoic age is related to a marginal portion of a supposed granite pluton in the zone of the Ten'kinskii deep fault. The deposit was formed during the collisional evolutionary episode of the Yana–Kolyma foldbelt. The deposit is hosted mostly in volcano-sedimentary rocks and is characterized by a complicated polygenetic evolution, which occurred in several stages. Most who studied this deposit share the opinion that it is of metamorphic–hydrothermal type. The ores of the deposit affiliate with the gold–quartz association of the low-sulfide gold–quartz–arsenopyrite type.

In spite of its remarkable diversity, the ore mineralization of this uniquely large deposit occurs as a structurally coherent and uniform orebody, which comprises quartz, quartz–sulfide, and quartz–carbonate veins and veinlets and accumulations of stringer and stringer-disseminated ores. The orebody was traced for a length of 5 km along its strike and has a width of 1 km. It is hosted by Late Permian rocks, mostly mudstone, siltstone, and silty clayey shale with rare sandstone and gritstone beds containing elevated carbon concentrations.

More than 70 minerals have been identified at the deposit. The most abundant gangue mineral is quartz (70–80%), carbonates and feldspars are less ubiquitous (20–30%), and still less common gangue minerals are albite and sericite. The most widely spread ore minerals are arsenopyrite and pyrite, and the less abundant ones are pyrrhotite, galena, sphalerite, scheelite, chalcopyrite, native gold, ilmenite, and rutile (1–3%). The geology, mineralogy, and geochemistry of the deposit and its genesis are described in (Goncharov et al., 2002).

METHODS

To study the structural and surface-bound modes of gold occurrence, V.L. Tauson and his colleagues have designed a technique of statistical samplings of analytical data on single crystals, which is referred to as SSADM (Tauson et al., 2001, 2002; Tauson and Luste-

nberg, 2008). The technique was further upgraded and improved and was successively applied in studying the structural and surface-related modes of occurrence of Au-accompanying elements, such as Ag, Sb, As, Bi, Cu, Mn, Ni, and B (Tauson et al., 2014). In the course of our research, we applied SSADM to study the modes of “invisible” Au, Pt, and Pd in arsenopyrite from the Natalkinskoe deposit.

Platinum and palladium were analyzed in solutions produced by decomposing single arsenopyrite crystals, after preparatory extraction concentrating and separating from the matrix. The extractant was tristyrylphosphine (C_6H_5CH-CH)₃P. Extraction was conducted from 0.5 M HCl solutions, the extractant concentration was 0.05 M (in toluene), and the contact time was 30 min. The volume ratio of the organic and aqueous phases was 2 : 1. Extraction was conducted in static regime at room temperature, without adding labializing agents. To change the concentrations of the elements, we used an organic phase. The analyses were carried out by atomic absorption spectrometry with electrothermal atomization on Perkin-Elmer 503 and AAnalyst-200 spectrophotometers.

RESULTS AND DISCUSSION

Data obtained by analyzing the concentrations of equidistributed Au, Pt, and Pd and on the proportions of their structural and surface-bound modes in arsenopyrite from the Natalkinskoe deposit are presented in Figs. 1–3 and Table 1. All of the dependences thus obtained for the average concentrations of elements in the sampling on the specific surface area of an average crystal are highly determinate ($R^2 = 0.86–0.99$), i.e., yield the following concentrations of the structural mode in a hypothetical infinite crystal: 0.01–6.77 ppm Au, 15.5–32.3 ppm Pt, and 0.63–2.6 ppm Pd. The average concentrations of the surface-bound modes of the elements (Table 1) are 6.1–30.4 ppm Au, 244–581 ppm Pt, and 26.6–82.1 ppm Pd.

SEM examination of the surfaces of sulfide minerals from the Natalkinskoe deposit (samples M-129/10 and M-161/10) confirms that Au and Pt are contained on the surface of arsenopyrite crystals. We found small (1 μ m and smaller) carbonate inclusions containing up to 1.09% Au and up to 0.81% Pt. The study was carried out using a Quanta 200 (FEI) scanning electron microscope equipped with a EDAX (United States) X-ray analytical setup at the Institute of Limnology, Siberian Branch, Russian Academy of Sciences.

Elevated Au, Pt, and Pd concentrations in the surface layers of arsenopyrite crystals from sample M-129/10 were confirmed by LA-ICP-MS analyses at the Vinogradov Institute. The analyses were conducted on a NexION 300D (Perkin Elmer) quadrupole ICP-MS equipped with a NWR-213 laser ablation system (wavelength 213 nm, laser beam 5 μ m in diameter). In this technique, the laser burns

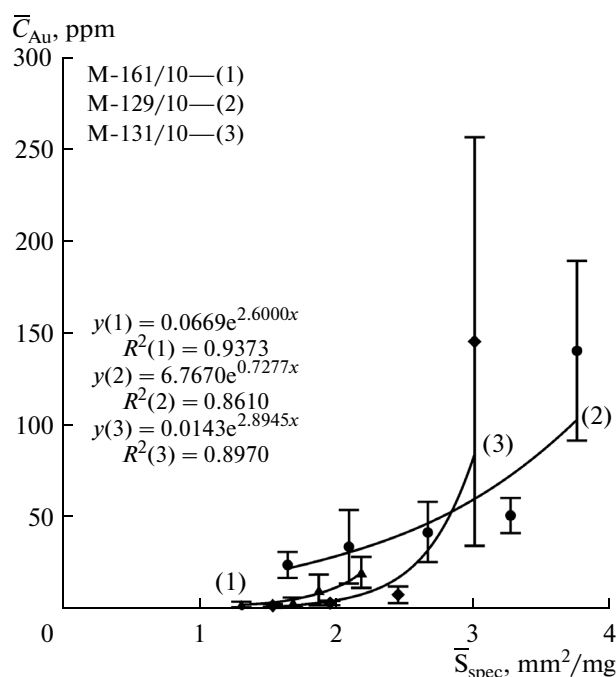


Fig. 1. Dependence of the average concentrations of equidistributed Au on the specific surface of an average crystal in the grain-size sampling from three arsenopyrite samples (M-161/10, M-129/10, and M-131/10) from mineralized veins at the Natalkinskoe deposit. Here and in Figs. 2 and 3, the curves are exponential approximations (the correlating equations are written to the left of the curves) of data points. The preexponential factor is an estimate of the structural Au admixture (in Figs. 2 and 3, same for Pt and Pd).

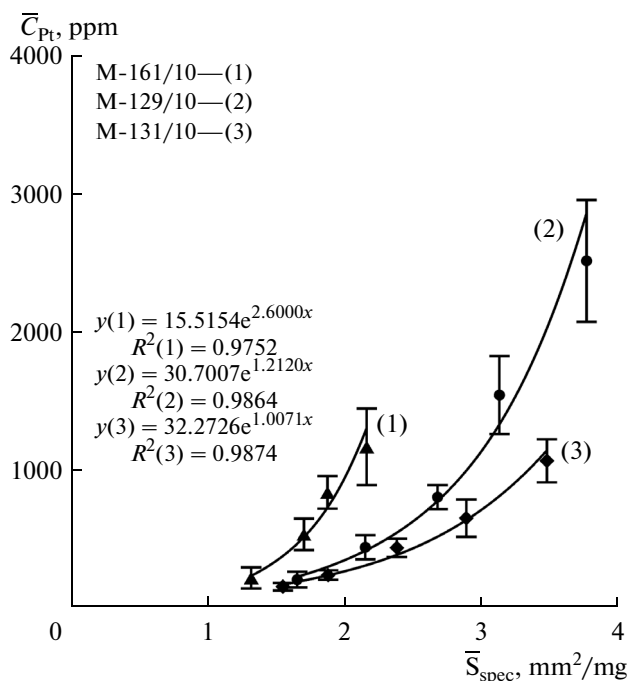


Fig. 2. Dependence of the average concentrations of equidistributed Pt on the specific surface of an average crystal in the grain-size sampling from three arsenopyrite samples (M-161/10, M-129/10, and M-131/10) from mineralized veins at the Natalkinskoe deposit.

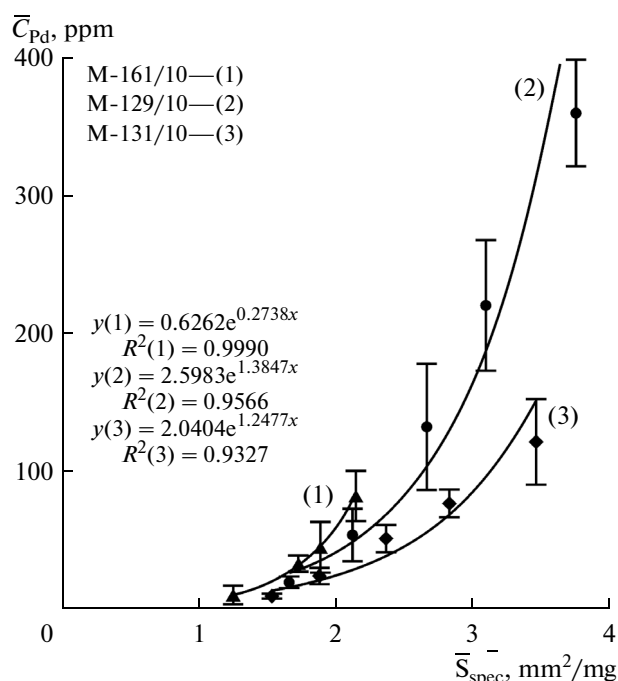


Fig. 3. Dependence of the average concentrations of equidistributed Pd on the specific surface of an average crystal in the grain-size sampling from three arsenopyrite samples (M-161/10, M-129/10, and M-131/10) from mineralized veins at the Natalkinskoe deposit.

a continuous groove 1 mm long on the crystal surface. The pilot burning of the samples with subsequent measuring the length of the groove under a SMM-2000 scanning electron microscope in atomic-force mode at the Vinogradov Institute made it possible to construct a profile for the dependence on the probing depth in the sample. A single laser pass yielded 100 nm analysis depth in arsenopyrite. Figure 4 shows the distribution of (a) Au, (b) Pt, and (c) Pd in the surface layer of one of the arsenopyrite crystals.

Platinum and palladium display an obvious tendency toward concentrating in the outermost 0–100 nm surface layer in arsenopyrite crystals. Gold shows a nearly parabolic dependence, which is likely explained by the fact that the maximum concentrating due to surface enrichment is not the only one, and the plot passes through another maximum, which is lower and may be explained by micro- and nanometer-sized Au⁰ inclusions. The occurrence of micrometer-sized Au inclusions on the surface of arsenopyrite was confirmed by X-ray microprobe analyses (Fig. 5), which were conducted on a JXA-8200 (JEOL, Japan) equipped with EDS and WDS, using proprietary software for semiquantitative and quantitative analysis, at the Vinogradov Institute.

The association of native gold with arsenopyrite is the most typical in the ores of the Natalkinskoe deposit. Native gold grains of various size (mostly small, 10–70 μm) form aggregates with arsenopyrite

Table 1. Analyses of size-fraction samplings of individual arsenopyrite crystals from the Natalkinskoe deposit

Sample	Number of crystals (starting and final samplings)	Final sampling						Concentration, ppm*			
		number of crystals	range of crystal masses, m	\bar{m} , mg	\bar{r} , mm	\bar{S}_{spec} , mm ² /mg	$\bar{C}_{\text{Au}} \pm \Delta$, ppm	\bar{C}_{tot}	\bar{C}_{equ}	C_{str}	\bar{C}_{sur}
Gold											
M-161/10	40-24	7	0.40–0.62	0.56	0.451	2.179	20.0 ± 8.4	18.9	6.0	0.07	6.12
		6	0.66–1.01	0.88	0.524	1.872	10.4 ± 8.4				
		5	1.03–1.39	1.23	0.587	1.681	3.7 ± 2.7				
M-129/10	43-26	6	1.42–4.31	2.61	0.754	1.307	2.3 ± 1.5	55.9	37.3	6.77	30.43
		7	0.10–0.12	0.11	0.262	3.745	141 ± 49				
		4	0.13–0.24	0.17	0.304	3.262	51.0 ± 9.5				
		5	0.27–0.37	0.31	0.371	2.664	41.9 ± 16.4				
M-131/10	53-33	5	0.48–0.73	0.64	0.472	2.089	33.9 ± 20.0	62.6	19.6	0.01	17.05
		5	1.01–1.45	1.30	0.597	1.645	24.0 ± 7.0				
		11	0.10–0.32	0.21	0.324	3.000	146 ± 111				
		7	0.34–0.52	0.40	0.404	2.448	7.8 ± 4.5				
		7	0.54–1.05	0.79	0.507	1.952	3.3 ± 1.1				
8	1.07–2.15	1.61	0.642	1.536	1.9 ± 0.8						
Platinum											
M-161/10	40-31	7	0.40–0.62	0.58	0.456	2.151	1168 ± 278	565	497	15.5	494
		8	0.66–1.01	0.90	0.529	1.866	838 ± 118				
		9	1.03–1.39	1.20	0.582	1.694	532 ± 114				
M-129/10	42-35	7	1.42–4.31	2.58	0.751	1.312	216 ± 75	669	606	30.7	581
		9	0.10–0.12	0.11	0.262	3.745	2519 ± 443				
		7	0.13–0.24	0.19	0.314	3.114	1543 ± 282				
		6	0.27–0.37	0.31	0.371	2.664	802 ± 87				
		8	0.48–0.73	0.59	0.459	2.143	438 ± 86				
5	1.01–1.45	1.30	0.597	1.645	202 ± 58						
Platina											
M-131/10	53-39	9	0.10–0.17	0.14	0.284	3.456	1067 ± 157	320	274	32.3	244
		6	0.18–0.32	0.24	0.339	2.873	649 ± 136				
		8	0.34–0.52	0.43	0.412	2.369	436 ± 67				
		7	0.54–1.05	0.88	0.524	1.872	236 ± 35				
		9	1.07–2.15	1.58	0.637	1.541	152 ± 28				
Palladium											
M-161/10	40-24	8	0.40–0.62	0.58	0.456	2.151	82.8 ± 18.2	38.7	31.0	0.63	31.4
		5	0.66–0.98	0.85	0.518	1.894	45.5 ± 18.3				
		6	1.00–1.32	1.12	0.569	1.734	33.6 ± 5.9				
M-129/10	41-31	5	1.38–4.31	2.87	0.777	1.262	10.9 ± 6.8	96.7	83.2	2.6	82.1
		9	0.10–0.12	0.11	0.262	3.745	361 ± 39				
		6	0.13–0.24	0.20	0.321	3.091	221 ± 47				
		5	0.27–0.37	0.31	0.371	2.664	133 ± 46				
M-131/10	52-38	6	0.48–0.73	0.60	0.461	2.125	54.4 ± 19.1	31.8	28.4	2.04	26.6
		5	1.01–1.45	1.25	0.590	1.671	20.3 ± 4.3				
		8	0.10–0.17	0.14	0.284	3.456	122 ± 31				
		6	0.18–0.32	0.26	0.350	2.827	77.4 ± 10.2				
		8	0.34–0.52	0.43	0.412	2.369	51.9 ± 9.9				
8	0.54–1.05	0.87	0.523	1.886	24.8 ± 6.0						
8	1.07–2.15	1.58	0.637	1.541	10.2 ± 1.8						

* \bar{C}_{tot} is the average concentration $\Sigma C_i m_i / \Sigma m_i$, \bar{C}_{equ} is the average concentration of equidistributed element in all samplings, C_{str} is the concentration of the structural mode (extrapolation of \bar{S}_{spec} to zero), \bar{C}_{sur} is the average concentration of the surface-bound mode.

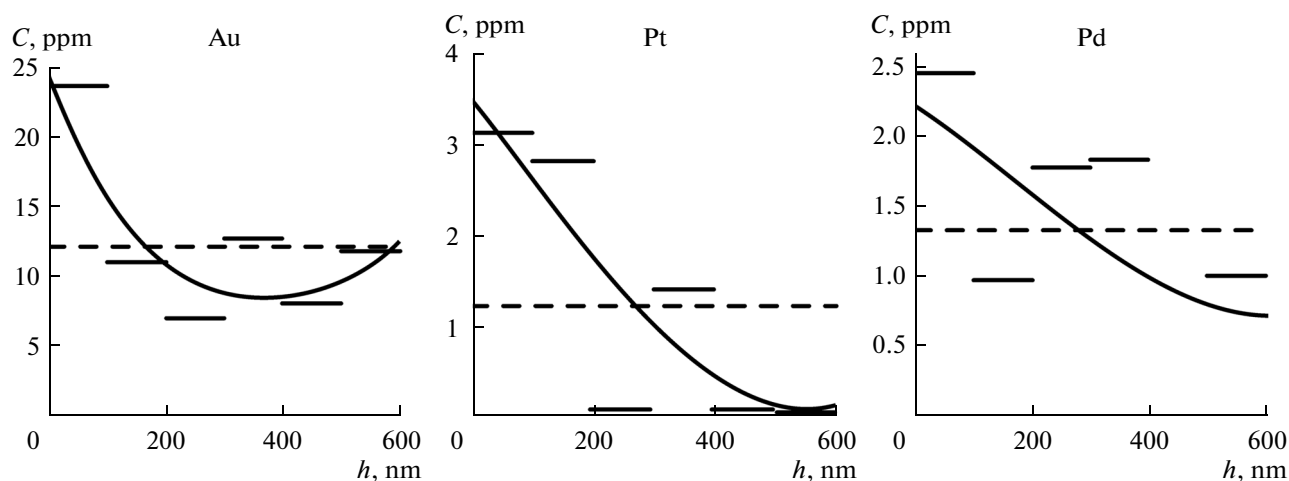


Fig. 4. Distribution of Au, Pt, and Pd concentrations in the surface layer of an arsenopyrite crystal: LA-ICP-MS data. Sample M-129/10 from the Natalkinskoe deposit. The dashed horizontal line indicates the average concentration of the element in the examined layer (0–600 nm), continuous heavy horizontal lines show the average concentrations of the elements in the layers 0–100, 100–200, 300–400, 400–500, and 500–600 nm.

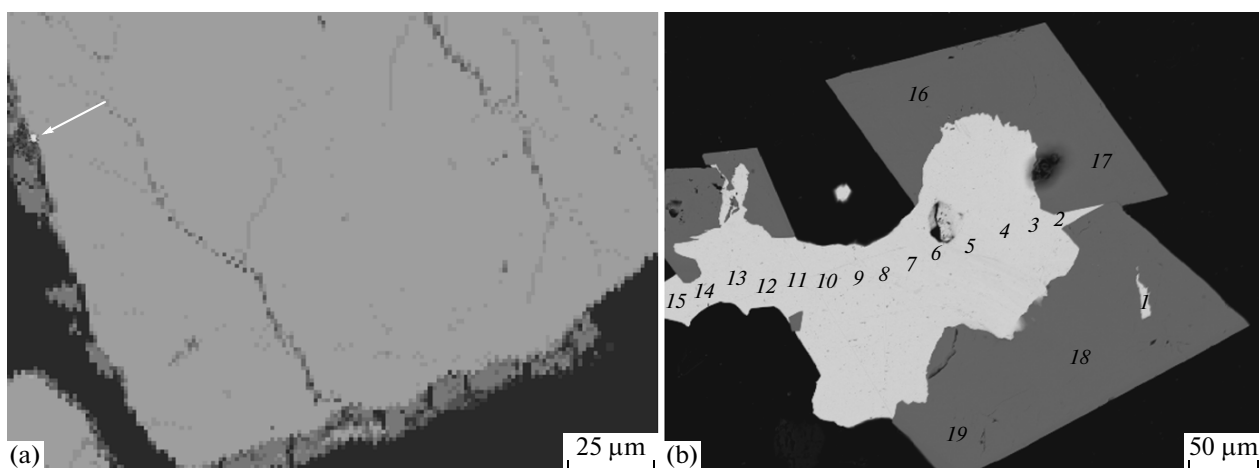


Fig. 5. Back-scattered electron images (JXA-800, JEOL, Japan, microprobe) of (a) fragment of an arsenopyrite crystal (gray) with a small gold inclusion (bright white speck corresponding to a grain 1–2 μm across) on a crystal face (indicated with an arrow), semi-quantitative EDS analysis with the use of proprietary JEOL software; (b) small gold inclusion (spot 1) and a large chunk of native gold (spots 2 through 15) in association with arsenopyrite crystals (spots 16–19); 1–19 are analytical spots (same as in Table 2), quantitative WDS analyses with the use of proprietary JEOL software.

and were found as small disseminated inclusions (<10 μm). The fineness of the gold varies insignificantly, from 770 to 800‰. Along with finely divided and fine gold (<10 and 10–70 μm , respectively), larger gold grains (up to 250 μm , Fig. 5, Table 2) occasionally occur in association with arsenopyrite. More rarely gold was found as an admixture. The only minor element always found in the arsenopyrite is Mo, and an Ag admixture is ubiquitous only locally (Table 3).

Note that the numerical data on the PGE concentrations (first of all, those of Pt) are inconsistent with atomic-absorption analyses (processed according to the SSADM procedure) and LA-ICP-MS analyses. In this

context, it should be stressed that the LA-ICP-MS data should be regarded as provisional. Moreover, any comparison of the LA-ICP-MS and SSADM data can hardly be warranted because the former pertain to very small analytical spots on the crystal surface and the latter were obtained on the sample as a whole, which usually comprised at least 40 individual crystals. Correspondingly, the amount of the material to be analyzed is a few picograms in the former instance and as much as tens of milligrams in the latter. It is also possible that the layer of a FeAsS crystal that is strongly enriched in PGE is even thinner or may be unequally distributed in the crystals, because of which its thickness is estimated with

Table 2. Composition of a small gold inclusion in an arsenopyrite crystal and a large grain of native gold in association with arsenopyrite

<i>n</i>	Ag	As	Fe	Au	S	Σ
1	20.954	<0.35	<0.33	79.046	<0.28	100
2	22.880	<	<	77.120	<	100
3	19.988	<	<	80.012	<	100
4	21.575	<	<	78.425	<	100
5	22.280	<	<	77.720	<	100
6	22.990	<	<	77.010	<	100
7	20.683	<	<	79.317	<	100
8	19.834	<	<	80.166	<	100
9	21.239	<	<	78.761	<	100
10	22.220	<	<	77.780	<	100
11	20.600	<	<	79.400	<	100
12	19.591	<	<	80.409	<	100
13	21.422	<	<	78.578	<	100
14	22.301	<	<	77.699	<	100
15	20.102	<	<	79.898	<	100
16	<0.49	50.744	30.026	<0.54	19.230	100
17	<	49.499	30.471	<	20.030	100
18	<	50.103	30.213	<	19.683	100
19	<	49.805	30.530	<	19.665	100

The numbers *n* of analytical spots are the same as in Fig. 5; concentrations of elements are in wt %; the sign “<” denotes concentrations below detection limits. Radiation intensity was measured and concentrations of elements were calculated using a JXA-8200 (JEOL, Japan) microprobe equipped with an energy-dispersive spectrometer and the proprietary software. No Se, Hg, Sb, Pb, Zn, Cu, Bi, Pt, Pd, Os, Ir, Ru, Rh, Ce, and La were detected, other elements marked with the sign “<” were not analyzed.

Table 3. Composition of arsenopyrite from the Natakinskoe deposit

<i>n</i>	Mo	Ag	As	Fe	Au	S	Σ
1	0.29	<0.10	50.49	34.26	0.36	15.19	100.59
2	0.26	<0.10	51.09	33.74	<0.14	15.98	101.08
3	0.27	<0.10	49.08	33.01	0.36	17.45	100.17
4	0.29	<0.10	46.43	34.33	<0.14	20.48	101.53
5	0.24	0.85	43.80	31.30	4.21	20.46	100.86
6	0.29	<0.10	46.85	33.76	<0.14	20.58	101.50
7	0.31	<0.10	48.78	30.56	<0.14	20.78	100.45
8	0.27	<0.10	49.74	31.38	<0.14	18.08	98.47

Numerals *n* correspond to the numbers of analytical spots on arsenopyrite crystals, concentrations of elements are in wt %, “<” denotes concentrations below the detection limits. Radiation intensity was measured and concentrations of elements were calculated using a JXA-8200 (JEOL, Japan) microprobe equipped with an energy-dispersive spectrometer and the proprietary software.

a significant error. Both of these hypotheses await their testing.

The fact that arsenopyrite concentrates Au, Pt, and Pd is confirmed by atomic-absorption analyses for these elements conducted in 10- to 20-mg samples. Preliminary data on the Au, Pt, and Pd concentrations in monomineralic fractions of arsenopyrite from the Natakinskoe deposit are reported in Table 4. The maximum Au concentrations (up to 1383 ppm) were found in the fines (<0.25 mm) and corroborate data that the association with arsenopyrite is dominated by finely divided and fine gold (<10 and 10–70 μm, respectively), which normally strongly enriches these fractions. The relatively homogeneous distribution of the concentra-

tions of Pt (23.0–62.4 ppm) and Pd (2.3–9.5 ppm) in various arsenopyrite fractions (<1, 0.25–0.5, and <0.25 mm) likely stems from the fact that both Pt and Pd occur in arsenopyrite in a non-mineral mode.

The enrichment of the surface of pyrite in certain minor elements (As, Cd, Cu, and Zn) was earlier proved by LA-ICP-MS analyses of material from mine tailings at the Kristineberg Zn–Cu deposits in northern Sweden (Öhlander et al., 2007). It seems to be quite probable that mine tailings at the Natakinskoe deposit can be strongly enriched in Au, Pt, and Pd contained in arsenopyrite fines.

At magmatic Cu–Ni deposits bearing PGE, the latter are usually accommodated in the structures of major

Table 4. Au, Pt, and Pd concentrations (ppm) in various fractions of arsenopyrite crystals from the Natalkinskoe deposit: data of atomic absorption analysis

No.	Sample	Description	Au	Pt	Pd
1	M-129/10	Arsenopyrite (−1 mm)	3.3	23.0	3.5
2	M-131/10	Arsenopyrite (+0.5 mm ...−1 mm)	4.3	24.2	2.8
3	M-131/10	Arsenopyrite (+0.25 mm ...−0.5 mm)	1.5	25.5	2.3
4	M-131/10	Arsenopyrite (+0.14 mm ...−0.25 mm)	3.2	29.3	3.6
5	M-161/10	Arsenopyrite (−1 mm)	1.3	26.9	3.7
6	M-161/10	Arsenopyrite (+0.5 mm...−1 mm)	19.0	47.1	6.3
7	M-161/10	Arsenopyrite (+0.25 mm ...−0.5 mm)	28.4	62.4	9.5
8	M-161/10	Arsenopyrite (+0.14 mm ...0.25 mm)	1383	43.6	6.2

Table 5. Structural characteristics of some Fe and Pt sulfides and arsenides

Mineral, its formula and structure	Bond	Bond length, nm
Pyrite FeS ₂ <i>Pa</i> 3	S–S Fe–S	0.226 0.208
Arsenopyrite FeAsS <i>P2</i> ₁ c	Fe–S Fe–As S–As	0.225 0.235 0.233
Platarsite Pt(As,S) ₂ <i>Pa</i> 3	Pt–As,S As,S–As,S	0.242 0.229
Sperrylite PtAs ₂ <i>Pa</i> 3	Pt–As As–As	0.249 0.241

sulfides (pyrrhotite and pentlandite), and lesser amounts of these elements occur in the form of individual minerals. Arsenic-bearing minerals that crystallized from sulfide melt served as high-capacity accumulators of PGE and Au, which is reportedly explained (in the most general form) by the strong chemical affinity between As and PGE (Dare et al., 2007). It is still uncertain whether As continues to show this feature in postmagmatic systems. Based on the data presented above for the Natalkinskoe deposit, we are prone to believe that these considerations are also pertinent to hydrothermal arsenopyrite. This follows from, for example, high concentrations of structural Pt and Pd (15.5–32.3 and 0.6–2.6 ppm, respectively). Table 5 lists the atomic spacing values in the structures of certain Fe and Pt sulfides and arsenides. Platarsite and sperrylite have pyrite-type structures (Szymański, 1979), with Fe–S and Pt–S, As spacing differing from the S–S, As and S–As, S ones by no more than 7 and 10%, respectively, which the difference even smaller (1.7%) for the arsenopyrite structure (Table 5). No such phases are known so far for Pd. In any event, the possible isomorphism of Pd in arsenopyrite seems to be limited.

The reason for the strong Pt and Pd enrichment in the surface layer seems to be analogous to that of Au in pyrite (Tauson et al., 2011, 2014). This may be chemical modification and structural restoration of the surface

layer of the crystal in the form of a nonautonomous phase. Because the stability field of arsenopyrite is adjacent to that of pyrite, according to the principle of continuous origin of phases on mineral surfaces and correspondence to the chemical speciation of elements on them (Tauson, 2009), the nonautonomous surface phase may have a defective structure of pyrite. Platarsite has the same structure (Table 5), and this ensures Pt accommodation in the surface phase.

It should be stressed that we were the first to detect the two modes of occurrence (structural and surface-bound ones) of equidistributed Au, Pt, and Pd in arsenopyrite. Equidistributed Au, Pt, and Pd seem to occur in a mode accommodated on the surface of nanometer-sized crystals of a nonautonomous phase. The latter is likely accommodated in the very thin (~100 nm) surface layer of the crystal. Studying this phase by electron microscopic and scanning microprobe techniques is currently in progress.

The structural modes of Au, Pt, and Pd (first and foremost Au) are also very important, in spite of their very low concentrations as compared to the concentrations of the surface-bound modes. By analogy with pyrite, only this mode can be used as an indicator of the activity of the element in hydrothermal solution. It has previously been proved that only the structural component of Au admixture in pyrite can be utilized to esti-

mate the Au concentration in the mineral-forming solutions. Data on structural Au make it possible to compare the concentrations of this element in ore-forming fluids at Au deposits (Tauson et al., 2011, 2014).

CONCLUSIONS

In spite of the relatively small number of samples in our selection, which could seem to be insufficient to comprehensively enough study ore mineralization at such a giant ore deposit as Natalkinskoe, we obtained results interesting in both the academic and the applied aspects.

Our data are the first to demonstrate that arsenopyrite from this gold deposit host equidistributed Au, Pt, and Pd in two major non-mineral modes: structural and surface-bound ones. It was proved that, similar to pyrite, high Au, Pt, and Pd concentrations in non-mineral modes in arsenopyrite are mostly related to the surface of crystals. Neither Pt nor Pd individual minerals were identified, whereas native Au is the most abundant (although not the only one) mode of occurrence of this element. The surface-bound mode of Au occurrence has an average concentration of ~6–30 ppm and is contained in virtually all arsenopyrite crystals, i.e., it likely makes up a significant part of the total Au amount contained in the ores. The situation with Pt and Pd is different: arsenopyrite is not the only concentrator, and also likely not the dominant one.

Our data confirm the ability of arsenopyrite to concentrate minor elements, first of all those apt to be accommodated in the mineral in relation to defects in its crystalline structure (including those at crystal surfaces). This important fact should be taken into account, for example, in processing ores containing sulfides, arsenopyrite in this instance. Similar to pyrite, gold-bearing arsenopyrite likely accommodates admixtures in compliance with a single universal mechanism, in which surface defects of crystals play an active role. In view of this, so-called refractory Au can be studied without destructing the structure of this mineral.

Small- and ultrasmall-sized gold particles, which are no larger than 10 μm , often cannot be recovered by means of direct cyanation, and hence, the processing of such ores required more complicated and expensive technologies. The nature of this gold is, however, not uniform, and distinguishing between gold modes contained in sulfide crystals and on their surfaces offers an approach to solving two problems. First, it is evaluating the amount of gold that cannot in principle be recovered without complete disintegration of the mineral structure. This, in turn, offers the possibility of predicting the amount of unrecoverable gold lost to tailings and makes it possible not to search for means of complete gold recovery if this is not warranted economically. The second problem is estimating an optimal size of grains to which the ore should be crushed and which corresponds

to the size of originally formed grains of mineral containing the desired component. This leads to optimization of energy and time consumption and in order not to excessively crush ore material if the valuable component is known to be contained in the surface layers of mineral grains.

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