

Noble Metals in Carbon-Rich Metamorphic Rocks of the Khanka Terrane, Primorie

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Abstract—Carbon-rich metamorphic rocks of Riphean age in the northern part of the Khanka terrane were first analyzed for concentrations of noble metals (Au, Ag, Pt, Pd, Ir, Os, and Ru). According to the data of various physicochemical analytical techniques, the Au and Pt concentrations broadly vary: from 0.01 to 52 ppm for Pt and from 0.1 to 30 ppm for Au. Various techniques of sampling and analysis variably affect the losses of these metals because of difficulties in the decomposition of metal–carbon chemical bonds. The carbon isotopic composition (^{13}C from -8.5 to -8.7%) of the graphitized amphibolite-facies rocks widespread in the core of the Ruzhino paleodiapir suggest that their carbon is of mantle provenance. The Early Cambrian metaterigenous rocks metamorphosed to the greenschist facies have ^{13}C from -19.9 to -26.6% , which testifies to its organic origin. The elevated concentrations of noble metals in these rocks suggest that the sources of carbon and metals were polygenetic and that the ore-forming system evolved over a long time span.

Keywords: noble metals, carbon, graphite, metamorphism, black shales, Khanka terrane, Primorie, Russian Far East.

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INTRODUCTION

Au–PGE ore mineralization is currently known to widely occur in carbonaceous shales in the Russian Far East, but the industrial development of these deposits is hampered by the lack of reliable analytical techniques and technologies for ore processing and the extraction of noble metals from these ores. These metals were also found in carbon-rich metamorphic complexes in the northern part of the Khanka terrane, where we detected elevated concentrations of Au and Pt at graphite deposits of the Tamga–Turgenevo group [17]. It should be mentioned that large graphite deposits have been known and mined in the area between the Tamga and Kedrovka rivers since 1945 [15], but have never before been examined for contents of noble metals because of the absence of their macroscopically discernible modes of occurrence. Our research was centered on the elucidation of the Au and PGE distributions in the rocks of the Ruzhino occurrence and the identification of their possible relations with the processes of graphitization.

GEOLOGICAL OVERVIEW AND METAMORPHIC PROCESSES

The Khanka Massif was long believed to be cratonic, but newly obtained geological evidence led to its classification with Caledonian folded structures [10, 15]. The Khanka Caledonides are a continuation of the Central Asian Orogenic Belt, to which such giant Au and Pt

deposits as Muruntau and Kumtor are spatially restricted.

The age of rocks composing the Khanka Massif remains largely uncertain, with the dates ranging from the Archean to Early Proterozoic. The latest data on the Sm–Nd systematics of the highest grade metamorphic rocks of the Khanka Massifs yielded a Middle Riphean age [10]. These rocks show traces of an early episode of regional metamorphism of low-gradient broad-zone type to the epidote-amphibolite and amphibolite facies, which was dated at 730 Ma. The late episode of metamorphism ranging from the greenschist to granulite facies was related to collisional events at the Cambrian–Ordovician boundary. The complexes were subdivided into rock series according to their metamorphic grades (Fig. 1). The highest-grade metamorphic rocks of the Imanskaya Group are metamorphosed to the amphibolite and low grades of the granulite facies. The younger rocks of the Ussuri Group were affected by metamorphism of the amphibolite and epidote-amphibolite facies. The metamorphism of the rocks of the Lesozavodskaya Group corresponded to the low-temperature epidote-amphibolite and greenschist facies. The terrigenous rocks of the Orlovskaya Group were metamorphosed to the greenschist facies. The upper part of the stratigraphic section of the metamorphic complex was dated at the Early Cambrian and consists of clayey and black phyllite shales, metaterigenous rocks, spillites, quartzites with Fe–Mn ore mineralization, and carbonate rocks, i.e., a rock assemblage typi-

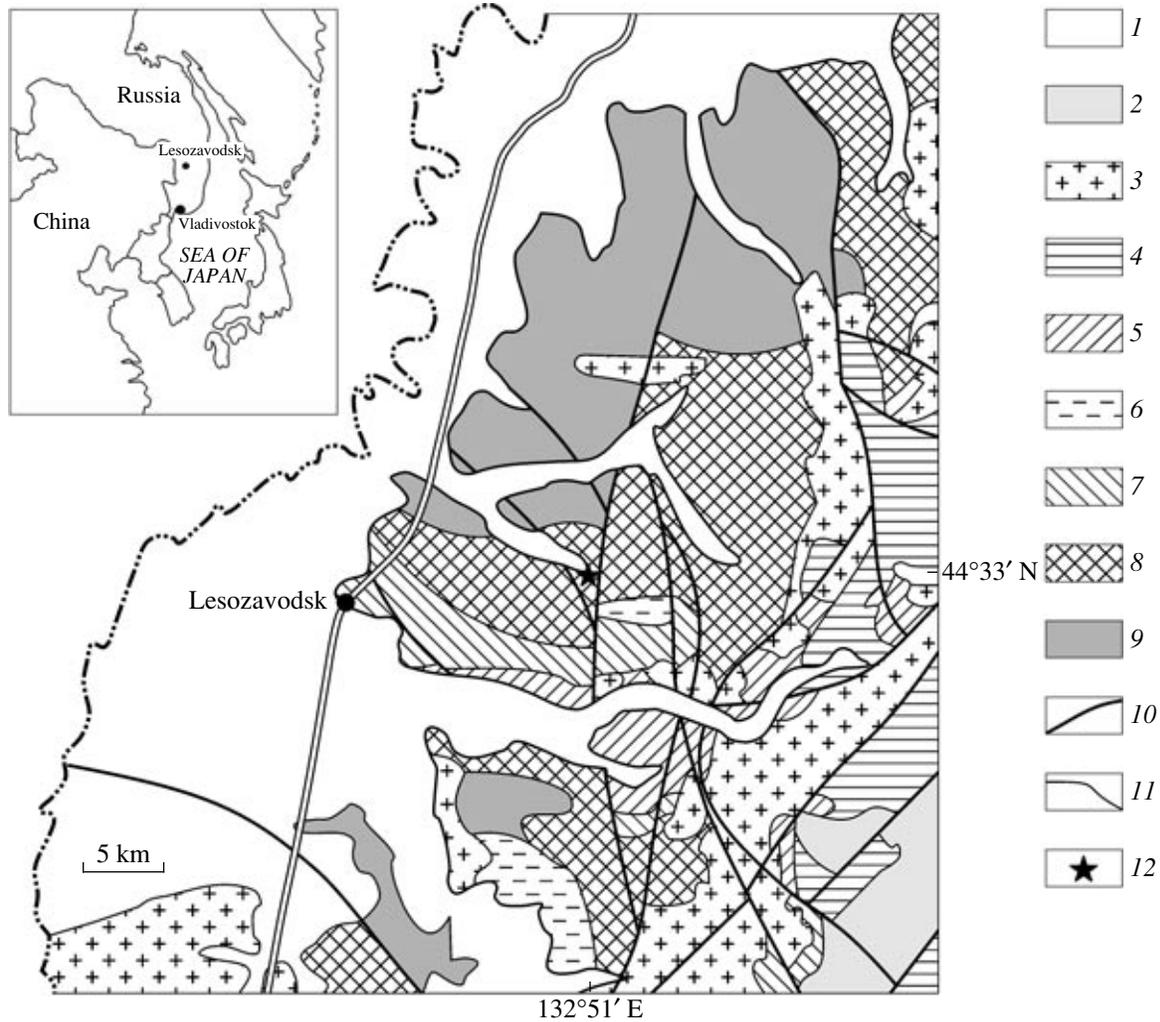


Fig. 1. Schematic geological map of the northern part of the Khanka terrane (prepared with the use of materials of V.I. Rybalko and A.N. Naidenko).

(1) Cenozoic deposits; (2) Early Cretaceous deposits; (3) Paleozoic and Mesozoic gabbro–granite complexes; (4) Paleozoic deposits; (5) Cambrian deposits of the Orlovskaya Group; (6) Early Paleozoic granitoids of the Ussuri Complex; (7–9) Proterozoic deposits: (7) Lesozavodskaya Group, (8) Ussuri Group, (9) Imanskaya Group; (10) faults; (11) geological boundaries; (12) Ruzhino ore field (44°33' N, 132°51' E).

cal accretionary prisms. The Precambrian rocks had an analogous original composition [16, 17].

The examined part of the Ussuri Group consists of intercalating biotite–feldspar–graphite, garnet–biotite–feldspar–graphite, and biotite–muscovite–feldspar schists and marbles with conformable injections of biotite and leucocratic granite–gneisses and with occasional thin (no thicker than 1 m) dikes of mafic–intermediate lamprophyres, which are conformable with the schistosity of the host rocks. The chemical compositions of the rocks are reported in Table 1. All lithological varieties are extensively graphitized, with graphite occurring in the form of fine-grained aggregates, monomineralic veins, and lens-shaped inclusions, which is reflected in the high carbon concentrations (from 6 to 39 wt %) of the rocks.

Along with their graphitization, the rocks of the Ussuri Group were affected by potassic metasomatism, which resulted in the development of veinlets and megacrysts of microcline and biotite. The rocks are also sometimes intruded by quartz and quartz–graphite veinlets that cut across the schistosity (Fig. 2) but contain no secondary sulfide mineralization, which is typical of complex Au–Pt deposits in black shales [5, 7]. The Ruzhino occurrence of ore mineralization is located in the core of a horst–anticline, whose limbs are made up a stratified sequence of quartz–graphite slaty black shales with high (25–30 wt %) carbon contents. These rocks are characterized by a more homogeneous distribution of the carbonaceous material, which also consists of graphite, according to X-ray diffraction data.

Table 1. Chemical composition of rocks from the Ruzhino ore field

Sample	02-1	02-3	02-4	03-1a	03-2a	03-3	03-3g	03-5
SiO ₂	70.82	34.74	66.50	38.61	50.54	38.56	52.05	39.39
TiO ₂	0.22	0.19	0.05	0.02	1.65	0.32	1.11	0.39
Al ₂ O ₃	12.61	12.03	12.33	20.19	20.51	8.95	20.27	8.88
FeO	0.26	5.50	0.16	0.64	7.90	0.85	6.50	0.78
Fe ₂ O ₃	0.32	0.29	1.65	0.69	1.50	2.18	3.60	2.84
CaO	3.04	0.20	0.28	4.12	3.71	2.51	2.14	2.51
MgO	0.32	0.58	0.62	0.56	3.67	2.16	3.74	2.16
MnO	0.02	0.03	0.01	0.02	0.18	0.06	0.20	0.05
Na ₂ O	0.95	0.93	1.90	2.18	4.07	1.83	3.13	1.72
K ₂ O	7.90	3.03	6.38	2.92	3.85	1.58	5.67	1.51
H ₂ O ⁻	0.10	0.59	tr	0.20	tr	tr	0.57	tr
H ₂ O ⁺	0.98	3.73	2.45	2.16	2.02	5.97	0.29	4.51
C	2.08	36.47	7.33	27.41	tr	34.57	0.62	33.84
S	0.04	0.53	0.01	0.01	0.03	0.04	0.01	0.04
Total	99.66	98.64	99.67	99.73	99.63	99.58	99.90	98.62

Note: Samples 02-1, 02-3, and 02-4 are graphitized leucocratic granite-gneisses; sample 03-1a is graphite metasomatic rock developing after biotite granite-gneiss; samples 03-2a and 03-3g are biotite--feldspar schist; sample 03-3 is garnet--biotite--feldspar--graphite schist; sample 03-5 is graphitized lamprophyre (conventional silicate chemistry analysis, analyst Zh.A. Shcheka).

In order to elucidate the nature of the regionally spread graphitization in the watershed area of the Tamga, Kabarga, and Kedrovka rivers, we determined the carbon isotopic composition of the rocks metamor-

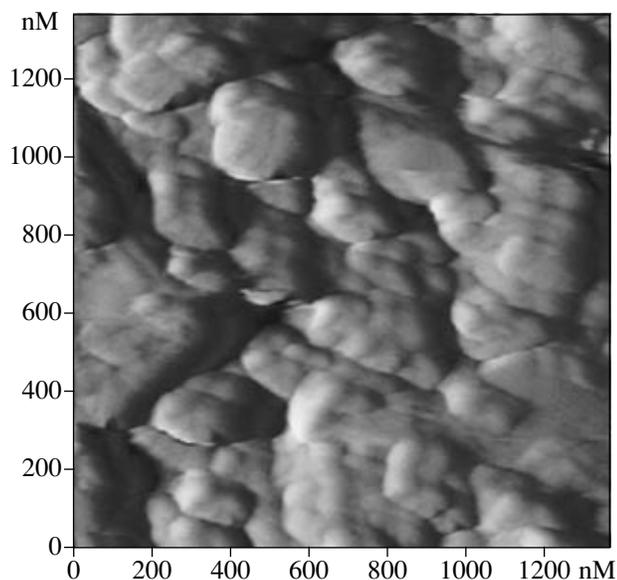
phosed to the amphibolite facies and the black shales metamorphosed to the greenschist facies. The $\delta^{13}\text{C}/\delta^{12}\text{C}$ ratios ($^{13}\text{C}_{\text{PDB}}$) were analyzed accurate to 0.1‰ on a Finnigan MAT-252 mass spectrometer at the

**Fig. 2.** Quartz–graphite veins in crystalline schists of the Ussuri Group.

Table 2. Carbon isotopic composition of graphite-bearing metamorphic rocks from the Ruzhino ore field

Sample	$\delta^{13}\text{C}_{\text{PDB}}$	Rock
Amphibolite facies		
02-1	-8.5	Graphite in granite-gneiss
02-4	-8.7	Plagioclase gneiss
03-1	-8.6	Biotite granite-gneiss
03-1a	-8.7	Graphite veinlet in gneiss
03-3	-8.6	Garnet-biotite-graphite schist
03-5	-8.5	Lamprophyre
Greenschist facies		
04-22	-19.9	Sericite-quartz-graphite schist
04-24	-19.3	Sericite-quartz-graphite schist
04-17	-25.2	Phyllitic shale
04-34	-23.7	Phyllitic black shale
04-40	-26.6	Black slaty shale

Analytical Center of the Far East Geological Institute, Far East Division, Russian Academy of Sciences. This ratio in the samples collected in the core of the paleodipir is characterized by insignificantly varying values within the range of -8.5 to -8.7% (Table 2). Such values characterize mantle carbon sources [4], which is corroborated by the extensive development of monomineralic graphite along the splay faulting and fracturing zones of deep faults. The mantle provenance of carbon during the degassing of the mantle also follows from the occurrence of globular microtextures, which were detected in the rocks examined under a Solver scanning atomic force microscope (Fig. 3). It is known that the

**Fig. 3.** Nanometer-scale globular microtexture of graphite (sample 03-1a).

condensation of carbonaceous gases with decreasing temperature facilitates the formation of globular microtextures during the phase transition from the gaseous to solid states [18].

The carbon isotopic composition of our samples from the Orlovskaya Group shows broader ^{13}C variations: from -19.9 to -6.5% . These values indicate that the carbon is of organic origin, because the ^{13}C values in the range of -19.8 to -26.5 characterize the carbon of marine sediments [20]. It should be mentioned that the IR spectra of the graphite-bearing rocks suggest the absence of any organic complexes and amorphous carbon, which, in turn, indicates that the metamorphic grade of the rocks was fairly high and facilitated the transition of the carbonaceous matter into graphite.

Judging from the results of mineralogical thermobarometry, the metamorphic temperature of the amphibolite-facies rocks of the Ussuri Group was 570 – 620°C at a total pressure of 3 – 4 kbar [11]. The garnet-biotite assemblage from the Ruzhino occurrence (sample 03-3) was formed at 600°C , according to the garnet-biotite thermometer [21]. Microprobe analyses of biotite from these schists indicate that the mineral occurs in two generations: (i) groundmass biotite and this mineral in inclusions in garnet porphyroblasts, both having the composition $\text{K}_{1.02}\text{Mg}_{1.27}\text{Fe}_{1.33}\text{Ti}_{0.2}\text{Al}_{1.62}\text{Si}_{3.0}\text{O}_{12}(\text{OH})_2$, and (ii) biotite occurring in veinlets cutting across the schistosity, which is poorer in Ti and Fe and has the formula $\text{K}_{1.01}\text{Mg}_{1.69}\text{Fe}_{0.9}\text{Ti}_{0.02}\text{Al}_{1.92}\text{Si}_{2.95}\text{O}_{12}(\text{OH})_2$. The morphology of the biotite veinlets suggests that the second biotite variety was formed owing to potassic metasomatism. The garnet also occurs in two varieties. Biotite 1 coexists with more magnesian garnet $\text{Ca}_{0.16}\text{Mg}_{0.45}\text{Fe}_{2.27}\text{Mn}_{0.18}\text{Ti}_{0.01}\text{Al}_{2.0}\text{Si}_{3.0}\text{O}_{12}$, which composes the cores of porphyroblasts. Their outer zones also consist of garnet of the pyrope-andradite series but with a higher andradite content $\text{Ca}_{0.14}\text{Mg}_{0.38}\text{Fe}_{2.32}\text{Mn}_{0.16}\text{Al}_{2.0}\text{Si}_{3.0}\text{O}_{12}$, which reflects retrograde zoning. Graphite is stable under these conditions, and the transition of amorphous carbon into graphite occurs, according to experimental data, at 500°C and 1 kbar [12]. A higher fluid pressure than in the experiments (3 – 4 kbar) should have decreased the phase transition temperature of amorphous carbon.

ANALYSES FOR NOBLE METALS: METHODS AND RESULTS

The low concentrations of PGE in carboniferous rocks and the absence of individual minerals of these metals make their analysis significantly more difficult and reduce the list of analytical techniques applicable for these purposes. The occurrence of newly formed graphite over broad areas at the Khanka terrane further complicates this problem because of the high resistance of graphite to oxidation decomposition needed to release and extract noble metals [3]. In view of these considerations, in studying the Ruzhino ore field, we

Table 3. Concentrations (ppm) of Au and Pt in graphite-bearing rocks from the Ruzhino ore field

Sample	Au	Pt	Analytical technique	Rock
02-1	40	n.a.	ICP–AES	Granite-gneiss with graphite
02-3	13	4	IMS	Granite-gneiss with graphite
02-3	30	n.a.	ICP–AES	same
03-1a	5	16	IMS	Granite-gneiss
03-3	3	6.7	IMS	Garnet–biotite–graphite schist
03-5	5	52	IMS	Lamprophyre
04-7a	12	20	IMS	Outer skan with dispersed graphite
04-7a	1.04	1.15	AA	same
04-7b	12	14	IMS	Skarned marble
04-7b	0.16	1.51	AA	same
04-17	7.2	5	IMS	Sericite–quartz–graphite schist
04-17	0.66	1.30	AA	same
04-29	15	18	IMS	Lamprophyre
04-29	0.46	1.28	AA	same
04-40	17	24	IMS	Sericite–quartz–graphite schist
04-4	0.18	1.29	AA	same
04-9	2.2	3.3	IMS	Black shale, Tamga
04-9	0.14	0.82	AA	same

Note: Analytical methods: AA—AA-6200 spectrophotometer, ICP-AES—atomic emission spectroscopy; IMS—ion mass spectrometer; n.a.—not analyzed.

applied a number of physicochemical analytical techniques.

The first analyses of the rocks for Au and Pt were conducted by ion mass spectroscopy (IMS) at the Institute of Microelectronic Technology and Ultrahigh-Purity Materials, Russian Academy of Sciences, in Chernogolovka, Moscow oblast. This method was first applied to analyze nonconducting substances because of the use of an ion source of glow discharge at a hollow cathode [14]. This enabled us to obtain the spectra of noble-metal isotopes, including $^{194,195,196}\text{Pt}$, $^{191,193}\text{Ir}$, ^{192}Os , and ^{197}Au . The results of the IMS analysis are presented in Table 3 in comparison with analyses for Au and Pt on an atomic emission spectrometer with inductively coupled plasma and on an atomic absorber, which were conducted at the Analytical Center of the Far East Geological Institute, Far East Division, Russian Academy of Sciences. The concentration values obtained by the latter analytical methods, which require the long-lasting chemical preparation of the samples with their decomposition in strongly oxidizing compounds, occurred to be much lower than the values obtained by IMS, except only those on sample 02-3 (Table 3). This was likely caused by the presence of cluster modes of metal occurrence in graphite and strong metal–carbon chemical bonds, which resulted in metal losses as much as two orders of magnitude during acid leaching. The metals can be lost in the form of volatile carbonyls or carbonyl chlorides during the calcina-

tions of the samples in HClO_4 [1, 2]. In addition, some graphite is retained in the insoluble residue, and this also leads to appreciable losses of the metals.

In order to test whether noble metals are indeed bound to carbonaceous matter, we also analyzed the solutions obtained by the dissolution of the silicate material in aqua regia and HF. These solutions contain all components except graphite, which remains in the residue. The solutions analyzed on an AA-6200 spectrophotometer were proved to contain low Au concentrations and neither Pt nor Pd concentrations above the sensitivity of the analytical technique. The subsequent long-lasting decomposition of the graphite residues, which were preliminarily calcinated at 600°C , in HClO_4 and HF allowed us to determine Au concentrations of up to 16.68 ppm, Pt up to 14.15 ppm, and Pd up to 5.67 ppm in some samples (Table 4).

Our data indicate that the noble-metal mineralization is closely related to graphite, and much metals is lost because of the release of volatile metal–organic complex compounds. Because of this, the decomposition of the “refractory” graphite-bearing rocks was conducted by the method of oxidizing fluorination by BrF_3 and KBrF_4 (this technique was developed at the Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences [9, 19]). An advantage of this method is its high selectivity and the degree of extraction of the elements to be analyzed. The analysis of 40 sample from the Ruzhino ore field determined the

Table 4. Concentrations (ppm) of noble metals in samples fractionated into a soluble constituent and graphite

Sample	Au*	Graphite**			ΣAu	C concentration, wt %	Rock
		Au	Pt	Pd			
02/1	0.73	16.68	8.68	5.67	17.41	35	Graphite metasomatic rock
02/3	0.56	2.83	2.15	0.99	3.39	~4.7	Plagioclase gneisses with graphite
02/4	0.61	4.18	2.39	1.23	4.79	~6.3	Granite-gneiss
03/1a	–	2.56	4.14	3.31	2.56	5.6	Graphite metasomatic rock
03/3	0.1	5.37	14.15	7.31	5.47	30	Garnet–biotite–graphite schist
03/5	1.26	0.04	4.46	1.24	1.30	29	Lamprophyre

*Au concentration in the dissolved silicate constituent was determined on an AA-6200 spectrophotometer.

**Au, Pt, and Pd concentrations in graphite calcinated at 600°C with subsequent decomposition and oxidation in HF and HClO₄ (for 30 days).

Table 5. Concentrations (ppm) of noble metals in diverse lithological varieties of rocks (data of atomic emission spectroscopy after oxidative fluoride decomposition)

Sample	Au	Pt	Pd	Ag	Rh	Ru	Ir	Os	Rock
04-13	1.89	1.08	0.13	0.81	–	0.015	0.003	0.014	Black shale
04-16	2.73	0.2	0.36	1.21	–	0.011	0.004	0.011	same
04-40	1.82	0.05	0.31	1.01	–	0.012	0.006	0.013	same
04-34	2.01	2.15	0.10	0.34	0.46	0.045	0.009	0.017	Lamprophyre
04-34a	2.23	1.41	0.14	0.27	0.74	0.035	0.015	0.017	same
04-29a	1.45	0.04	0.13	2.47	–	0.045	0.019	0.029	Skarnoid
04-77	1.43	1.99	0.45	4.41	0.08	0.08	0.02	0.02	same
04-1a	0.61	1.91	0.24	0.65	0.005	–	–	–	Plagioclase gneiss
04-33	0.77	2.56	0.38	0.67	–	–	–	–	Granite-gneiss
04-78	0.044	0.044	0.08	0.51	–	–	–	–	same
04-3	0.2	1.67	0.14	0.47	–	–	–	–	Skarn
04-82	0.18	0.03	0.36	1.65	–	–	–	–	same
04-107	0.29	0.08	–	0.31	–	–	–	–	Marble
04-7	0.22	1.44	0.17	1.10	–	–	–	–	Vein graphite
04-108	1.01	0.09	0.28	0.52	0.005	0.007	–	–	Vein quartz

presence of a broad spectrum of noble metals (concentrations in ppm): 0.021–3.57 Au, 0.2–4.41 Ag, 0.04–3.56 Pt, 0.02–0.55 Pd, 0.002–0.055 Ir, 0.011–0.09 Os, 0.007–0.2 Ru, and 0.001–0.74 Rh. The chemical preparation of the samples involved the decomposition of the pristine sample (3–5 g in mass) and its transformations into solid sulfates with the subsequent analysis of noble metals by atomic absorption spectroscopy (AES). Note that the whole spectrum of PGE was found in the black shales and lamprophyre dikes but was generally atypical of the granite-gneisses, marbles, and skarns (Table 5).

Replicate analyses of the same samples for Au were conducted by neutron activation (NAA) at the Institute of Chemistry, Far East Division, Russian Academy of Sciences. The samples intended for analysis were 0.5 kg in mass. The results of the analyses are listed in Table 6 (in comparison with the previous data) and

show consistent data on Au concentrations (within the analytical error and with an exception of only a few samples). The highest Au concentrations in some samples were determined only by NAA. The data presented in Tables 3–6 show significant discrepancies between the Au and Pt concentrations determined in rocks by various methods, perhaps, because of the different techniques used to prepare the samples for analyses that were coupled with various metal losses due to the release of volatile metal–organic complexes and the sometime incomplete graphite dissolution. The most realistic Au and Pt contents were determined by the physical methods of ion mass spectrometry and neutron activation analysis, which do not require any chemical preparation of the samples. IMS analyses for metals are conducted in small solid samples (no more than 100 mg), which results in the overestimation of metal concentrations in recalculation to one ton of the ore and, hence,

Table 6. Concentrations (ppm) of Au in graphite-bearing rocks from the Ruzhino ore field according to data of neutron activation analysis (NAA) and atomic emission spectroscopy (AES) with preliminary fluoride decomposition

Sample	NAA	AES	Rock
04-1	≤0.8	0.51	Plagioclase gneiss
04-1b	1.8	0.71	Graphite veinlet in plagioclase gneiss
04-2a	≤0.7	0.636	Biotite granite-gneiss
04-3	≤0.2	0.198	Pyroxene skarn
04-3a	≤1.0	0.876	Lamprophyre
04-5	2.6	0.2	same
04-7a	≤1.1	1.18	same
04-13	≤0.3	0.143	Skarnoid
04-16	0.9	1.89	Black shale
04-27	≤1.4	–	Plagioclase gneiss
04-28	≤0.7	0.23	same
04-29	15.2	1.73	Lamprophyre
04-33	0.4	0.774	Granite-gneiss
04-35	0.4	0.767	Plagioclase gneiss
04-40	0.4	1.82	Slaty shale
04-68	14.2	n.a.	Graphite metasomatic rock
04-73	0.8	0.03	Endoskarn
04-74	2.1	0.112	Graphitized plagioclase gneiss
04-75	1.6	–	same
04-77	≤0.5	0.05	Skarnoid
04-78	≤0.4	0.044	Granite-gneiss
04-80	0.9	0.37	Endoskarn with graphite
04-81	1.7	0.043	same
04-101	≤1.2	0.57	Lamprophyre
04-107	6.8	0.29	Marble with up to 7% graphite
04-107c	17.1	0.29	Marble with up to 30% graphite
04-108	0.5	1.01	Vein quartz

Note: NAA were conducted at the Institute of Chemistry, Far East Division, Russian Academy of Sciences (analyst V.V. Ivanenko); AES analyses were carried out at the Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk (analyst V.M. Mit'kin).

hampers the application of this method to the appraisal of overall metal reserves and resources. At the same time, it is advisable to use this method in the course of exploration for buried ore mineralization at extended fields of rocks with carbonaceous matter.

MINERALOGY AND GEOCHEMISTRY

Micrometer- and submicrometer-sized grains of native Au are often found in graphite masses. Microprobe analyses of individual gold grains reveal their high grades of fineness and narrow compositional vari-

Table 7. Microprobe analyses (wt %) of monazite (Mnz), magnetite (Mgt), and hypersthene (Hyp)

Element	Mnz	Mgt	Mgt	Mgt	Mgt	Hyp	Hyp
Na	0.19	0.14	0.12	0.19	0.33	0.38	0.36
Mg	–	0.24	0.20	0.43	0.36	0.18	0.17
Al	0.48	0.09	0.07	–	–	2.17	2.02
Si	3.87	2.74	2.33	2.68	2.26	19.53	18.07
P	7.29	0.01	0.01	–	–	0.39	0.17
Cl	0.17	0.18	0.16	0.09	0.08	0.36	0.34
K	0.22	0.03	0.03	0.03	0.04	0.13	0.12
Ca	9.14	0.73	0.64	0.53	0.46	3.06	2.84
Ti	0.29	0.05	0.04	0.10	0.09	0.02	0.02
Cr	–	–	–	0.16	0.15	0.15	0.14
Mn	–	0.20	0.19	0.07	0.06	–	–
Fe	5.08	69.97	61.92	69.71	61.37	34.74	32.43
Sr	0.24	0.11	0.10	–	–	–	–
La	3.92	0.35	0.32	0.49	0.44	–	–
Ce	1.55	0.12	0.11	0.27	0.23	0.08	0.17
Pr	0.46	–	–	0.06	0.05	0.32	0.39
Nd	1.20	–	–	0.26	0.24	0.48	0.45
Pt	–	0.09	0.08	0.20	0.17	–	–
Pb	0.24	0.36	0.32	0.26	0.22	0.55	0.51
Au	–	–	–	–	–	0.15	0.13
Th	39.32	–	–	0.20	0.10	0.52	0.48
O	26.35	24.05	32.94	24.05	33.28	36.55	40.99
U	–	–	0.45	–	–	–	–
Total	100.01	99.46	99.58	99.78	99.91	99.76	99.80

ations: 79.27–97.16 wt % Au and 3.3–22.02 wt % Ag. We did not detect any visible modes of PGE occurrence, neither were they identified under an electron microscope. The graphite typically abounds in inclusions of ore and accessory minerals: magnetite, pyrite, zircon, thorite, monazite, native Cu, Y–Th–P phases, Cu–Sn and Cu–Sn–Fe alloys, and, more rarely, arsenopyrite.

A broad spectrum of trace elements (Ba, Sr, Cu, Zn, Hg, Ni, Cr, Ti, V, Mn, W, Zr, La, Ta, Nb, and Re) was detected by XRF in the graphitized rocks from the Ruzhino ore field. The highest concentrations of these elements are typical of the lamprophyres, which contain up to 1 wt % of these elements (including Hf, Tb, Y, U, As, Cd, and Er, which are absent from other rocks). Along with them, the rocks contain volatile components: 100–400 ppm F, up to 40 ppm Cl, up to 0.48% P₂O₅, and 0.02–0.1% SO₃, whose presence confirms the possibility of gas transport reactions.

Inasmuch as elevated PGE concentrations were found in lamprophyre dikes, we attempted to identify minerals concentrating these elements. For this pur-

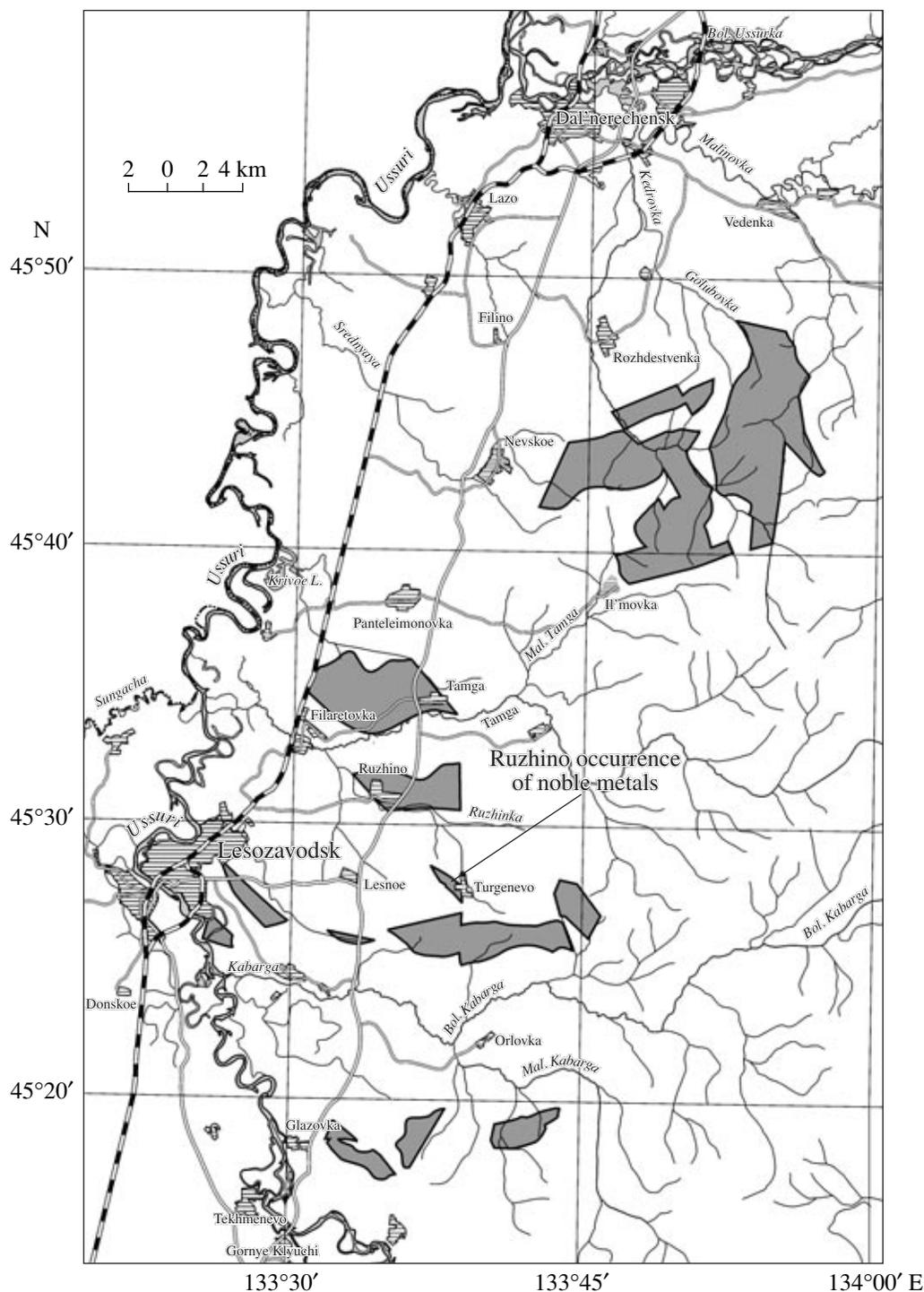


Fig. 4. Location map of regionally spread graphitization fields (gray) in the northern part of the Khanka terrane (prepared with the use of materials of the Primorye Geological Survey).

pose, the samples were examined on a CamScan MV 2300 microprobe with a beam 157–200 nm in diameter at the Institute of Experimental Mineralogy, Russian Academy of Sciences, in Chernogolovka, Moscow oblast. Table 7 lists the concentrations of some elements in minerals from sample 03-5, which were calcu-

lated by the INCA Energy 200 computer program. All of the analyzed magnetite grains turned out to bear Pt, and its concentration is positively correlated with REE concentrations, a fact that rules out a random character of the analytical results. No Pt was detected in any other phases, including the accessory monazite, thorite, and

orthite. Gold was found only in hypersthene. The occurrence of Pt and Au in the magnetite and hypersthene implies their magmatic source.

The lamprophyres have a porphyritic texture, with insets commonly consisting of mafic minerals, such as hypersthene, diopside, and biotite, and accounting for up to 55% of the rock by volume. The groundmass consists of potassic feldspar and plagioclase (An_{45-47}) with minor amounts of thin-prismatic hornblende (no more than 2%) and quartz (no more than 3%). Graphite is unevenly distributed in the rocks and occurs as fine-crystalline masses, dust, and veinlets. Its contents in the lamprophyres vary from 3 to 30%. The chemical composition of the lamprophyres is presented in Table 1.

CONCLUSIONS

Carbon-rich rocks in the northern part of the Khanka terrane are characterized by regionally spread graphitization, which is associated with elevated contents of noble metals. The regional character of graphitization in metamorphic complexes is typical of the northern part of the terrane, from Glazovka to Rozhdestvenka (Fig. 4). It is pertinent to mention that the areas of extensive graphitization are cluster along a submeridional (northeast-trending) line, whose trend coincides with the submeridional trends of deep faults and associated fault structures. This provides additional support of the idea that the graphitization processes involved deep carbon.

The problem of metal incorporation in the structure of carbonaceous matter is actively discussed in the literature [1, 8, 13]. Experimental data indicate that the graphite structure includes stable metal-carbon bonds, which are formed when aromatic structures lose their hydrogen ions during metamorphism [12]. Metals thereby "intrude" the deformed rings in place of hydrogen ions in the hexagons [1]. This idea receives support from the results of studying Au cluster modes in graphite-bearing ores from several widely known gold deposits. The analysis of extensive electron-microscopic material reveals accumulations of spherical gold-organic protoclusters between the layers of the graphite structure [8]. The spherical shapes of the clusters, in which metal-organic and graphite layers alternate, explains their stability during the thermal treatment of graphite-bearing samples and the difficulties in determining these metals by modern analytical techniques because of the oxidation and destruction of metal-carbon bonds.

The protoliths of our rocks from the central part of the paleodiapir were mostly of magmatic genesis and were metamorphosed to the amphibolite and epidote-amphibolite facies. Along with regionally spread carbonation, these rocks were also affected by intense metasomatic feldspathization and biotitization. The ore-hosting complex shows the following features typ-

ical of noble-metal deposits in zones of mantle-crustal diapirism:

- (1) a significant vertical extents of the noble-metals and graphite ore mineralization;
- (2) the spatial restriction of the ore-hosting rocks to horst-anticline structures that have folded-blocked structures and are lithologically heterogeneous;
- (3) the occurrence of granitoids of various composition and lamprophyre dikes conformable with the schistosity;
- (4) the close association of the noble-metal mineralization with carbonaceous matter and the presence of heavy carbon isotopes of mantle origin;
- (5) the presence of geochemically diverse elements (Au, Ag, W, Ta, Rb, Hg, Re, Bi, Cu, Pt, Pd, Os, Ir, Co, Ni, Ti, U, Sr, etc.) in the ores;
- (6) the absence of individual PGE minerals in the rocks;
- (7) the weak hydrothermal sulfidization and silification of the rocks;
- (8) traces of pneumatolitic-hydrothermal carbonation in the rocks.

The carbonaceous-silicic metasomatic rocks (so-called fluidizites) often have a schistose texture and can hardly be distinguished from black shales. These rocks are commonly mapped as slate-phyllite shale zones at the limbs of thermal dome structures [3].

These features are typical of deposits attributed to the fluid-magmatic genetic type [3, 6, 7]. According to the aforementioned researchers, these unusual deposits are formed with the participation of magmatic, metamorphic, and metasomatic processes in relation to long-lived mantle-crustal diapirs. The sources of carbon and metals were mantle-crustal metasomatic processes, which were spatially restricted to developing deep faults and related crustal deformations.

The weak oxidation and sulfidization of the rocks and the reduced conditions during the process of carbonation and gas transport reactions (which were favorable for the release of metals from the deep-seated source) predetermined the absence of individual PGE minerals in the rocks of the Ruzhino ore field. The genesis of the native gold was related to the instability of gold carbonyls under the metamorphic conditions. The decomposition of these compounds during heating in the course of metamorphic and metasomatic processes resulted in the transition of the gold from an excited to a normal state [6]. The gold chemically bound to aromatic hydrocarbons in benzene structures formed more stable metal-carbon bonds, which were not broken during metamorphism until temperatures as high as 500°C [12]. Because of this, the ores also contain native gold. Because of their aforementioned features, the Ruzhino ores are "refractory," and the extraction of noble metals from them is laborious and costly. Noble metals are unevenly distributed in the rocks of various lithological compositions, which makes it even more difficult to

outline the most promising high-priority areas. The elevated Au and Pt contents determined in some samples and the extensive development of carbonaceous rocks (and their high thicknesses, up to 3000 m and occasionally even more) suggest that the resources of noble metals can be economic. Their appraisal requires detailed exploration and prospecting operations at the fields of carbonaceous rocks, including the metaterrigenous rocks of the Mitrofanovskaya and Orlovskaya formations.

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REFERENCES

1. N. K. Bel'skii, L. A. Nebol'sina, I. G. Oksenoid, et al., "Decomposition of Samples for Platinum Assaying in Carbonaceous Rocks," *Zh. Anal. Khim.* **52** (2), 150–153 (1997).
2. G. M. Varshall, T. K. Velyukhanova, and A. V. Korochantsev, "On Relationship between the Noble Metal Sorption Capacity of Carbonaceous Substances and Their Structure," *Geokhimiya*, No. 8, 1191–1199 (1995).
3. S. F. Vinokurov, Yu. N. Novikov, and A. V. Usatov, "Fullerenes in the Geochemistry of Endogenic Processes," *Geokhimiya* **35** (9), 937–944 (1997) [*Geochem. Int.* **35** (9), 822–828 (1997)].
4. E. M. Galimov, A. G. Mironov, and S. M. Zhmodik, "Nature of Carbonization in the Carbon-Rich Rocks of the Eastern Sayan," *Geokhimiya* **38** (4), 355–360 (2000) [*Geochem. Int.* **38** (4), 317–322 (2000)].
5. D. A. Dodin, N. M. Chernyshov, and B. A. Yatskevich, *PGM Deposits* (Nauka, St. Petersburg, 2000) [in Russian].
6. P. F. Ivankin and N. I. Nazarova, *Procedure for Metalliferous Structures Investigation in Terrigenous Sequences* (Nedra, Moscow, 1988) [in Russian].
7. A. F. Korobeinikov, *Non-Conventional Multicomponent Gold-Platinum Group Metal Deposits in Foldbelts* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 1999) [in Russian].
8. V. N. Matvienko, Yu. D. Kalashnikov, and V. A. Narseev, "Clusters: The Protoform of Precious Metals Occurrence in Ores and Mineralized Rocks," *Rudy Met.*, No. 5, 28–36 (2004).
9. V. N. Mit'kin, L. M. Levchenko, A. I. Khanchuk, and G. G. Likhoidov, "Assaying of Noble Metals in Black Schist Samples from Metalliferous Deposits in East Siberia, Russian Northeast, and Maritime Region by Oxidative Fluorination," in *Proceedings of Scientific Conference, Irkutsk, Russia, 2005* (Irkutsk, 2005), Vol. 2, pp. 228–231 [in Russian].
10. M. A. Mishkin, A. I. Khanchuk, D. Z. Zhuravlev, and S. I. Lavrik, "First Data on the Sm–Nd Systematic of Metamorphic Rocks in the Khankai Massif, Primor'e Region," *Dokl. Akad. Nauk* **374**, 813–815 (2000) [*Dokl. Earth Sci.* **375** (8), 1283–1285 (2000)].
11. L. L. Perchuk, M. A. Mishkin, A. R. Kotelnikov, et al., "Thermodynamic Conditions of Metamorphic Rocks in the Khankai Massif," in *Essays on Physicochemical Petrology* (Nauka, Moscow, 1980), No. 9, pp. 139–167 [in Russian].
12. L. P. Plyusnina, T. V. Kuz'mina, and O. V. Avchenko, "Experimental Modeling of Gold Sorption on Carboniferous Component for 20–500°C, 1 kbar," *Geokhimiya* **42** (8), 864–873 (2004) [*Geochem. Int.* **42** (8), (2004)].
13. É. A. Razvozhzaeva, A. N. Spiridonov, V. D. Tsykhan'skii, et al., "Platinum in Carbonaceous Components of the Sukhoi Log Deposit," *Geol. Geofiz.* **43**, 286–296 (2002).
14. G. G. Sikharulidze, "Ion Source with a Hollow Cathode for the Elemental Analysis of Solid Bodies," *Mass-Spektrometriya* **1** (1), 21–30 (2004).
15. V. P. Solonenko, *Geology of Graphite Deposits in East Siberia and Russian Far East* (Izd. Geol. Literaturny, Moscow, 1951) [in Russian].
16. A. I. Khanchuk, V. V. Ratkin, and M. D. Ryazantseva, *Geology and Mineral Resources in Primorye* (Dal'nauka, Vladivostok, 1995) [in Russian].
17. A. I. Khanchuk, L. P. Plyusnina, and V. P. Molchanov, "First Data on Gold-Platinum Group Metal Metallization in Carbonaceous Rocks of the Khangai Massif, Primorye," *Dokl. Akad. Nauk* **397** (4), 524–529 (2004) [*Dokl. Earth Sci.* **397**, 820–824 (2004)].
18. N. P. Yushkin, A. I. Pavlishin, and A. M. Askhabov, "Ultradispersed State of Minerals and Problems of Nanomineralogy," *Miner. Zh. Kiev* **25** (4), 7–31 (2003) [in Russian].
19. V. N. Mitkin, A. A. Galizky, and T. M. Korda, "Some Observations on the Determination of Gold and the Platinum-Group Elements in Black Shales," *Geost. Newslett.* **24**, 227–240 (2000).
20. A. S. Naidu, R. S. Scalan, and N. M. Feder, "Stable Organic Carbon Isotopes in Sediments of the North Bering–South Chukchi Seas, Alaskan–Soviet Arctic Shelf," *Continental Shelf Res.* **13**, 669–691 (1993).
21. L. L. Perchuk and I. V. Lavrentieva, in "Experimental Investigation of Exchange Equilibrium in the System Cordierite–Garnet–Biotite," in *Advances in Physical Geochemistry* (Springer Verlag, New York, 1983), pp. 199–239.