Arizona Geological Society Digest 22
2008

Prospects for noble-metal deposits in graphite-bearing metamorphic rocks of the Khanka terrane, Russian Far East

A.I. Khanchuk, L.P. Plyusnina, and V.P. Molchanov
Far East Geological Institute, Russian Academy of Sciences, Vladivostok, Russia

ABSTRACT

The Khanka terrane in the Russian Far East has, for the first time, been studied for gold and PGE (platinum-group elements) content in carbon-enriched, metamorphic rocks of the Late Proterozoic - Lower Cambrian age. A complex sequence of alternating leucocratic granite-gneiss, biotite granite-gneiss, marble, biotite-feldspar-graphite, and garnet-biotite-feldspar crystalline schists, with concordant lamprophyre dykes, has undergone regional graphitization that has resulted in carbon contents as high as 36 percent. Gold (to 30 ppm) and platinum (to 52 ppm) values of potential economic interest were measured in all above mentioned rock varieties by ion mass-spectrometry (IMS), neutron-activation analysis (NAA), and atomic absorption spectroscopy (AAS). The isotopic composition of carbon in the graphite-bearing rocks of amphibolite facies was found to be unusually uniform (^{13}C = -8.5 to -8.7‰) that indicates an endogenic source. Along with graphitization, the regionally metamorphosed rocks in the Khanka terrane were affected by intense metasomatic feldspathization and biotitization. The protolith from the core of a diapiric fold is mainly of magmatic origin and has been metamorphosed to epidote-amphibolite, and amphibolite facies TP conditions. The Au-PGE-bearing complex reveals features typical of noble-metal deposits from magmatically derived fluids interpreted to be generated by mantle-crustal diapirism.

INTRODUCTION

Over the past decades there has been increasing interest in carbon-bearing rocks enriched with gold and platinum. The graphite-bearing metamorphic rocks of northern part of the Khanka terrane may also be considered as prospective for noble metals mineralization. It must be noted that large-sized graphite deposits of the Tamga-Turgenevo group have been known in the Russian Far East since 1945. However, the deposits have not been studied or evaluated for their noble metals content until recently. The purpose of this paper is to provide information about the noble metals content in the graphite-bearing metamorphic rocks of the region.

GEOLOGIC SETTING AND METAMORPHISM

The graphite-saturated metamorphic-rock sequence in the Ruzhino study area of the northern part of the Khanka terrane occurs between the rivers Kabarga, Tamga, Ruzhinka, and Kedrovka (Fig. 1). The lower part of the sequence has been subdivided into the following graphite-bearing series of Precambrian age in accordance with their metamorphism: 1) the highest metamorphic rank and presumed oldest, amphibolite to granulite facies Imanskaya series; 2) the epidote-amphibolite to amphibolite facies Ussuriiskaya series; 3) the greenschist to epidote-amphibolite facies Lesozavodskaya series; and 4) the greenshcist facies Orlovskaya series (Khanchuk et al., 2004a, b; Khanchuk et al., 2007). The upper part of the metamorphic complex is of Lower Cambrian age and consists of graphite-bearing phyllite, spilite, metasedimentary rocks, and quartzite alternating with ferromanganesian and carbonate rocks. Previously, the Khanka massif was assumed to be a craton. Recently obtained data, however, suggest its Caledonian folded nature (Mishkin et al., 2000; Khanchuk et al., 2004a, b). The Khanka Caledonides may be considered as an extension of the Central Asian orogenic belt, which hosts the giant

e-mail: Khanchuk: director@fegi.ru

Khanchuk, A.I., Plyusnina, L.P., and Molchanov, V.P., 2008, Prospects for noble-metal deposits in graphite-bearing metamorphic rocks of the Khanka terrane, Russian Far East, *in* Spencer, J.E., and Titley, S.R., eds., Ores and orogenesis: Circum-Pacific tectonics, geologic evolution, and ore deposits: Arizona Geological Society Digest 22, p. 181-185.

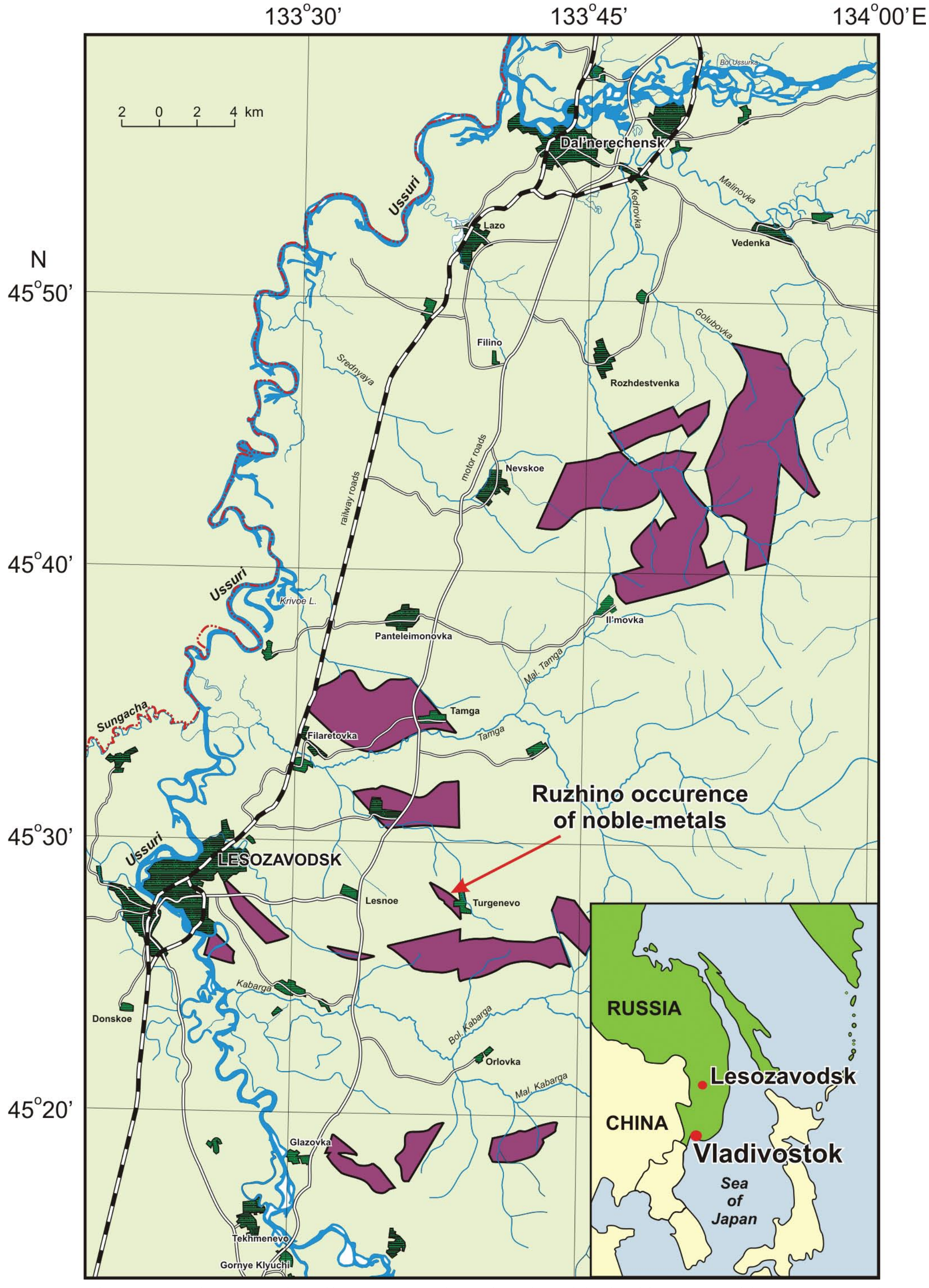

Fig 1. Location of regionally metamorphosed rocks with significant graphite content and Ruzhino study area (dark plots).

PGE-bearing gold deposits of Muruntau and Kumtor, which are hosted in carbonaceous rocks of Paleozoic age.

The age of the Khanka massif is debatable. Early interpretations suggested ages varying from the Archean to Proterozoic. The latest data, based on Sm-Nd systematics of the most metamorphosed rocks from the Khanka terrane, indicate their age as Middle Riphean (Mishkin et al., 2000). Approximately 730 million years ago, these rocks underwent low gradient, broadly zonal, regional metamorphism that reached epidote-amphibolite to amphibolite facies PT conditions. Later stages of regional metamorphism that ranged from greenschist to granulite facies PT conditions correlate with one or more collisional events that took place during Late Cambrian to early Ordovician time.

To research these rocks for possible noble-metals mineralization, the cross section of the metamorphic rocks located

Table 1. Gold and platinum content (ppm) in graphite-bearing rocks of Ruzhino Cross Section, Khanka terrane, Russian Far East

Sample	*Au*	*Pt*	*Method of assay*[1]	*Rocks*
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	skarn with dispersed graphite
	1.04	1.15	AAS	
04-7b	12	14	IMS	skarned marble with graphite
	0.16	1.51	AAS	
04-17	7.2	5	IMS	sericite-quartz black shale
	0.66	1.30	AAS	
04-29	15	18	IMS	lamprophyre with dispersed graphite
	0.46	1.28	AAS	
04-40	17	24	IMS	sericite-quartz black shale
	0.18	1.29	AAS	
04-9t	2.2	3.3	IMS	
	0.14	0.82	AAS	

[1] *IMS=ion mass spectroscopy; AAS=atomic absorption spectroscopy*

to the northwest of the village of Turgenevo, at the head of the Ruzhinka River valley, has been studied. Here the multiple-layered metamorphic complex, consisting of biotite-feldspar-graphite schist, garnet-biotite-feldspar-graphite schist, and marble, were intruded by biotite and leucocratic granite-gneiss. Marble near the granite gneiss were transformed into skarn. Concordant with foliation are thin (less than 1m wide), fault-controlled, lamprophyre dykes of gabbro-diorite composition. Graphite is widespread in all regionally metamorphosed rocks and occurs as monomineral veins and flattened lenses. The described metamorphic complex occurs in the core of the diapiric fold structure that is enveloped and flanked by quartz-sericite-graphite and phyllitic black shale alternating with carbonate and volcanogenic rocks. The flanking rocks of volcanogenic-terrigenous-carbonate parentage have been noticeably affected by secondary processes of sulfidization and silicification. In contrast, rocks near the core of the fold structure have undergone potassium metasomatism, resulting in the formation of metacrysts and veinlets of biotite and feldspar. All of the metamorphic rocks in the fold structure have undergone intensive graphitization, with carbon contents ranging up to 36 percent by mass.

Table 2. Concentrations (ppm) of PGEs and Ag in selected rock types of Ruzhino cross section, Khanka terrane

Sample	*Pt*	*Pd*	*Ag*	*Rh*	*Ru*	*Ir*	*Os*	*Rock*
04-13	1.08	0.13	0.81	-	0.015	0.003	0.014	black shale
04-16	0.2	0.36	1.21	-	0.011	0.004	0.011	
04-40	0.05	0.31	1.01	-	0.012	0.006	0.013	
04-34	2.15	0.10	0.34	0.46	0.045	0.009	0.017	lamprophyre
04-34a	1.41	0.14	0.27	0.74	0.035	0.015	0.017	
04-29a	0.04	0.13	2.47	-	0.045	0.019	0.029	skarnoid
04-77	1.99	0.45	4.41	0.08	0.08	0.02	0.02	
04-1a	1.91	0.24	0.65	0.005	-	-	-	plagiogneiss
04-33	2.56	0.38	0.67	-	-	-	-	granite-gneiss
04-78	0.044	0.08	0.51	-	-	-	-	
04-3	1.67	0.14	0.47	-	-	-	-	skarn
04-82	0.03	0.36	1.65	-	-	-	-	
04-107	0.08	-	0.31	-	-	-	-	marble
04-7	1.44	0.17	1.10	-	-	-	-	graphite vein
04-108	0.09	0.28	0.52	0.005	0.007	-	-	quartz vein

Table 3. Gold concentrations (ppm) in graphite-bearing rocks from Ruzhino cross section, measured by NAA and EC TEA AAS with preliminary fluorine decomposition.

Sample	*NAA*	*AAS*	*Rock*
04-1	≤0.8	0.51	plagiogneiss
04-1b	1.8	0.71	graphite veinlet in plagiogneiss
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	
04-7a	≤1.1	1.18	
04-13	≤0.3	0.143	skarnoid
04-16	0.9	1.89	black shale
04-28	≤0.7	0.23	plagiogneiss
04-29	15.2	1.73	lamprophyre
04-33	0.4	0.774	granite-gneiss
04-35	0.4	0.767	plagiogneiss
04-40	0.4	1.82	black shale
04-68	14.2	n/a	graphite metasomatic rock
04-73	0.8	0.03	skarn
04-74	2.1	0.112	plagiogneiss
04-77	≤0.5	0.05	skarnoid
04-78	≤0.4	0.044	granite-gneiss
04-80	0.9	0.37	skarn
04-81	1.7	0.043	
04-101	≤1.2	0.57	lamprophyre
04-107	6.8	0.29	marble with graphite about 7%
04-107c	17.1	0.29	marble with graphite about 30%
04-108	0.5	1.01	quartz vein

ANALYTICAL PROCEDURES

Normally low platinum-group element (PGE) concentrations in carbonaceous rocks and the absence of individual minerals of these metals make their analysis significantly more difficult and demand application of special physicochemical methods. Above mentioned graphite occurrence over a broad area of the Khanka terrane further complicates this problem because of the high resistance of graphite to oxidative decomposition needed for noble-metal extraction. In view of these considerations, a number of physicochemical analytical techniques have been applied to study the graphite-bearing rocks of the Ruzhino cross section.

Preliminary assay of the rocks for gold and platinum has been performed by ion mass spectroscopy (IMS). This method was first applied to analyze non-conducting solid substances owing to designing a new glow discharge ion source on the basis of a hollow cathode (Sikharulidze, 2004). The results of the IMS analyses are presented in Table 1.

For five samples, analytical values for Au and Pt were determined using both IMS and atomic-absorption spectroscopy (AAS) analytical techniques. The concentration values measured by AAS, which required the long duration of chemical preparation, have generally lower Au and Pt values than those obtained with the IMS analytical method.

Dissolution of the graphite-bearing rocks was conducted by the method of oxidizing fluorination using BrF_3 and $KBrF_4$ as decomposition reagents (Mitkin et al., 2000). An advantage of this method is its high degree of extraction of the elements to be analyzed by atomic absorption spectrophotometer and thermoelectric atomization with prior extract concentration (EC TEA AAS). Analysis of 40 samples from the Ruzhino study area has defined a broad spectrum of noble metals which varied broadly within the range (concentration in ppm): 0.021-3.57 for 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 more complete PGE spectra were found in the black shales and lamprophyre dykes, but were generally atypical of the granite-gneisses, marbles, and skarns (Table 2).

Replicate analyses of the same samples for gold were conducted by neutron-activation analysis (NAA). In Table 3, the results are listed in comparison with the data received by both NAA and EC TEA AAS analytical methods. The data presented in Tables 1-3 show significant discrepancies between noble-metal content determined by various methods, which apply a different sample preparation and instrumental assay. The authors judge that chemical oxidation of graphite leads to significant metal losses due to the emission of volatile metall-organic compounds. Therefore, higher gold and PGE contents can be determined by the physical analytical methods, i.e., the IMS and NAA methods, which do not require any chemical preparation of the samples.

MINERALOGY AND GEOCHEMISTRY

Thin flakes of native gold are noted by microscope within graphite veins, while no visible mineral PGE forms are found. Microprobe analysis of gold grains reveals the following fineness and compositional variations: 79.27 - 97.16 weight percent Au and 3.3-22.02 weight percent Ag. Numerous inclusions of ore and accessory minerals of micron and submicron sizes have been identified within graphite flakes by the high-resolution transmission electron microscopy (HRTEM). The inclusions identified include Th-bearing monazite, zircon, magnetite, barite, Y-Th-P minerals, Cu-Sn and Cu-Sn-Fe alloys, pyrite, and arsenopyrite. The enhanced content of rare and trace elements such as V, Ba, Sr, Cu, Zn, Pb, Sn, Hg, Ni, Cr, Mn, W, Zr, La, Ta, Nb, and Re was measured by the X-ray-fluorescence analysis (XRF). Accessory mineral content is especially high in lamprophyre dikes, which contain up to 1.0 wt. % rare-earth elements (REE), including also Hf, Tb, Y, U, Pr, Sm, and Er. In addition, the studied metamorphic rocks always contain volatile components; i.e., 100-400 ppm F, up to 40 ppm Cl, up to 0.48 percent P_2O_5 and 0.021 to 0.10 percent SO_3, whose presence confirms a possibility of gas transport reactions.

Carbon from lamprophyre and other graphite-bearing varieties from the Ruzhino study area has been analyzed for isotopes to help interpret the source of the graphite. The isotopic analyses were carried out by Finningan MAT–252 mass-spectrometer in Vladivostok. The accuracy of the isotopic ratio $^{13}C/^{12}C$ ($^{13}C_{PDB}$, ‰) measurements is ±0.1‰. The measurements of carbon isotopes in metamorphic rocks of amphibolite facies from the core of diapiric-fold structure produced rather uniform values ranging from -8.5 to -8.7‰. Such values are definitely characteristic of an endogenic source of carbon, evolving as a part of gaseous phases. A globular crystal microstructure of graphite from the studied rocks was detected by atomic-force microscope of the Solver series (Fig. 2). The globular form may be caused by gaseous condensation with lowering temperature. This conclusion is supported by the abundant development of graphite along the zones of jointing, dislocations, and deep-seated faults. The wider range of the ^{13}C values between -19.9 and -26.6‰ has been determined for graphite samples of black shale occurring at flanks of the diapiric fold structure and subjected to lower metamorphism of greenshist facies. These values indicate the organic nature of the carbon in the black shale because ^{13}C values between -21.2 to -26.5‰ are interpreted to be typical

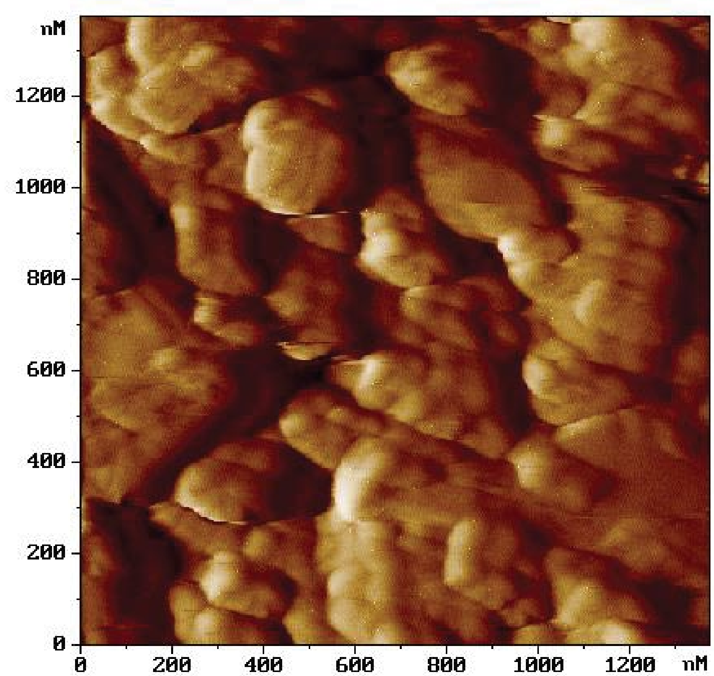

Fig 2. Nanometer-scale globular microtexture of graphite (sample 03-1a) examined with the Solver scanning atomic-force microscope.

of isotopic composition of organic carbon from sea floor sediments (Lewan, 1983).

No organic complexes or amorphous carbon in the rocks have been revealed in the IR-spectra, while graphite occurs in all metamorphic and igneous rocks of the region. This may be explained by high temperature regional metamorphism in the folded core of the Ruzhino study area. Khanchuk et al. (2007) report metamorphic temperatures estimates ranging from 600 -650°C as defined by biotite-garnet compositions in garnet-biotite-feldspar-graphite schist, according to the biotite-garnet geothermometer of Perchuk and Lavrentieva (1983). A further observation is that amorphous carbon transfers to graphite at the lower temperature of about 500°C at Pfl equal to 1 kb according to experimental data (Plyusnina et al., 2004).

SUMMARY

Carbon-rich rocks in the northern part of the Khanka terrane, specifically the Ruzhino study area, are characterized by regionally dispersed graphitization that is associated with elevated contents of noble metals. It is noteworthy that the areas of extensive graphitization are concentrated along regional fault structures, which supports the interpretation of an endogenic source for the elevated carbon and noble metal values.

In addition to regional graphitization, the rocks of the Ruzhino study area were also affected by intense metasomatic feldspathization and biotitization. The protolith from the core of the diapiric fold structure was mostly of magmatic genesis, which was metamorphosed to amphibolite and epidote-amphibolite facies. Thus, the graphite-bearing deposits were formed with participation of magmatic, metamorphic, and metasomatic processes during long-term evolution of the mantle-crustal diapir fold. The sources of carbon and metals were endogenous fluids evolving via regional faults associated with deep seated, crustal deformation.

Noble-metal deposits in black shale formations are frequently subjected to successive stages of metasomatism: the first, including graphitization and feldspathization, reflects reducing conditions. The second constitutes an oxidation stage in which metal-carbon bonds are broken down (Dodin et al., 2000). The weak degree of both oxidation and sulfidization of the rocks and the reduced conditions during the graphitization predetermined the absence of individual PGE minerals within the studied ore field. Native gold was found as microscopic gold particles up to 1 µm size in association with graphite. The visible gold formation was conditioned by instability of gold carbonyls under metamorphic conditions. This gold is accompanied by invisible gold, chemically bounded in benzene aromatic hydrocarbons. It forms more stable metal-carbonic bonds, which are not broken during metamorphism up to 500°C (Plyusnina et al., 2004).

Uneven distribution of noble metals in the metamorphic rocks of the Ruzhino study area induces some difficulties for outlining of the most prospective areas. The extensive areas of carbonaceous rocks, about 1000 km^2, and their thickness of up to 3000 m, suggest that resources of noble metals here can be potentially very significant. Their appraisal requires detailed geologic mapping and exploration of carbonaceous rocks, including the Cambrian metasedimentary rocks of the Orlovskaya Formation.

REFERENCES CITED

Dodin, D.A., Chernyshov, N.M., Yatskevich, B.A., 2000, Platinum-metal deposits in Russia: Nauka, Sankt-Peterburg, 729 p., (in Russian).

Khanchuk, A.I., Molchanov, V.P., and Plyusnina, L.P., 2004a, Gold-platinum mineralization in carbon-bearing rocks of Khanka Massif, *in* Khanchuk, A.I., ed., Tectonics, Magmatism, and Metallogeny: The Interim IAGOD Conference, Far East Geological Institute, Vladivostok, Russian Federation, p. 19-22, (in English).

Khanchuk, A.I., Plyusnina L.P., Molchanov V.V., 2004b, First data on gold-platinum group metal mineralization in carbonaceous rocks of the Khanka massif and prediction of a large noble metal deposit in Primorye: Doklady Earth Sciences, Nauka/Interperiodica, Moscow, v. 397, p. 820-824, (in English).

Khanchuk, A.I., Plyusnina, L.P., Molchanov, V.P., Medvedev, E.I., 2007, Noble metals in carbon-rich metamorphic rocks of the Khanka terrane, Primorie: Russian Journal of Pacific Geology, Moscow, Pleiades Publishing Ltd., v. 1, n. 1, p. 61-70, (in English).

Lewan, M.D., 1983, Effects of thermal maturation on stable organic isotopes as determined by hydrous pyrolusis of Woodford shale: Geochimica et Cosmochimica Acta, v. 47, n. 8, p.1471-1480.

Mishkin, M.A., Khanchuk, A.I., Zguravlev, D.Z., Lavrik, C.I., 2000, First data on Sm-Nd systematics of metamorphic rocks in the Khanka massif: Nauka/Interperiodica, Moscow, Doklady Earth Sciences, v. 374, p. 813-815, (in English).

Mitkin, V.N., Galizky, A.A., Korda, T.M., 2000, Some observations on the determination of gold and the platinum-group elements in black shales: Geostandards Newsletter, v. 24, p. 227- 240.

Perchuk, L.L., and Lavrentieva, I.V., 1983, Experimental investigation of exchange equilibria in the system cordierite-garnet-biotite, *in* Advances in physical geochemistry: New York, Springer Verlag, p. 199-239.

Plyusnina, L.P., Kuz'mina, T.V., Avchenko, O.V., 2004, Modeling of gold sorption on carbonaceous matter at 20-500°C: Geochemistry International, Nauka/Interperiodica, Moscow, v. 42, p. 755-763.

Sikharulidze, G.G., 2004, Ion source with hollow cathode for elemental analysis of solids: Mass-Spectrometry, v. 1, n. 1, p. 21-30, (in Russian).