МІНЕРАЛОГІЧНИЙ ЗБІРНИК MINERALOGICAL COLLECTION
2005. № 55. Вип. 1–2. С. 29–33 2005. N 55 (1–2). P. 29–33

УДК 549.2:552.4(571.63)

NOBLE METALS IN CARBON-BEARING ROCKS OF PRIMORYE

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The Khanka crystalline massif (Primorye) has been studied for gold and platinum content in graphite-bearing rocks. Chemical analysis of leucocratic granite-gneiss, gabbro-amphibolite, biotite-feldspar-graphite and garnet-biotite-feldspar slates, which have undergone regional graphitization, showed a high carbon content up to 29–36 mas. %. Gold (3–30 g/t) and platinum (4–52 g/t) contents of economic interest were measured in all abovementioned varieties. The isotopic composition of the carbon analyzed in 8 samples was found to be unusually uniform ($^{13}C_{PDB}$ = (–8,5)–(–8,7) ‰) which proves its mantle source. The obtained data suggest genetic correlation of gold-platinoid mineralization with regional graphitization, occured widely in the Middle-Riphean metamorphic complexes, which are located between the rivers of Kabarga, Tamga, and Kedrovka.

Key words: metamorphism, platinoides, gold, graphite, black shales, Primorye.

In recent decades nontraditional gold and platinoid deposits have been discovered in black shale formations of different age. Scientists are paying more and more attention to them, as in the 21st century it is believed that these deposits will provide the greatest portion of noble metals production [5]. This explains the necessity to search for new prospective rock complexes, such as the graphite saturated metamorphic sequence of the northern part of Khanka massif. It has been subdivided into the following graphite-bearing series in accordance with their metamorphism: the Imanskaya series metamorphosed in amphibolite facie (up to granulite facies), Ussuriiskaya one – in amphibolite, and epidot-amphibolite facies, Lesozavodskaya – in epidot-amphibolite and greenschist facies, and Orlovskaya – in greenschist facies. The upper part of the metamorphic complex has Lower Cambrian age and consists of clay and graphite-bearing slates, metaterrigenous rocks, spilites, and quartzites with ferromanganesian and carbonate rocks. Such variegated sequence of rocks like these is usually characteristic of accretion prisms. Similar initial composition characterizes the Pre-Cambrian formations as well [4].

For a long time the Khanka massif was assumed to be a craton. Recently obtained data, however, suggest its Caledonian folded nature [3]. The Khanka caledonides may be considered as an extension of the Central Asian orogenic belt, which hosts the giant gold and platinum deposits in carbon-bearing rocks of Muruntau and Kumtor.

The age of Khanka massif is debatable; different concepts suggest ages varying from the Archean to Lower Proterozoic. The latest data based on Sm-Nd systematization of the most metamorphosed rocks from the Khanka massif defined their age as Middle Riphean one [3]. Seven hundred thirty million years ago, these rocks underwent regional metamorphism of low-gradient and broad zonal type in epidote-amphibolite to amphibolite

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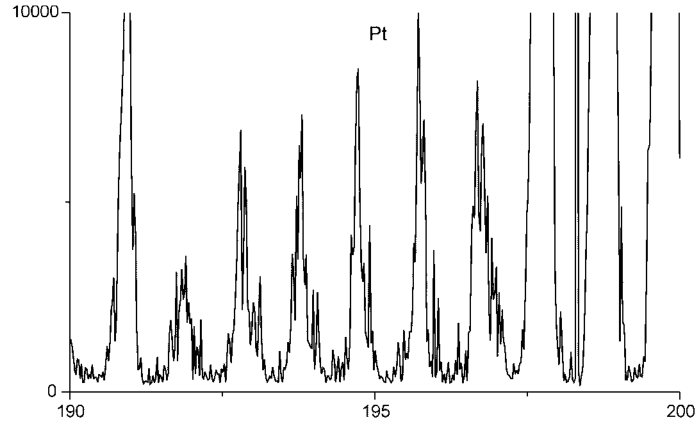
facies. The later stage of the metamorphism from greenshist to granulite facies correlates to collisions, which occurred at the Cambrian/Ordovician boundary.

To research these rocks for possible noble metal mineralization, the authors studied the cross-section of metamorphic rocks located to the north-west of the village Turgenevo, in the valley head of the Ruzhinka River. Here the multiple-bedded metamorphic complex of pyroxene gabbro-amphibolite, biotite-fieldspar-graphite and garnet-biotite-fieldspar-graphite shales is injected by leucocratic granite-gneiss. The last are considerably broken down and graphitized, and have no a contact influence on the host rocks. The graphite in them is dispersed or occurs as mono-mineral veins and flattened lens. The described metamorphic complex occurs in the core of a large thermal dome, being replaced by quartz-mica and graphite-quartz-sericitic phyllite-like shales at the flanks.

This cross-section is noteworthy by the lack of superposited processes of hydrothermal alteration (sulphidization, carbonatization, and others), usually observed in complex gold-platinoid deposits of folded belts [5]. At the same time, all types of the studied rocks underwent intensive graphitization. So, the chemically analyzed carbon content in graphite slate (sample 03-3), gabbro-amphibolite (sample 03-5), and graphite-bearing granite-gneiss (sample 03-1a) lies within the range 29–36 %. It must be noted that graphitization is developed on a regional scale throughout the area between the rivers Tamga, Kabarga, and Kedrovka that hosts the well-known graphite deposits of the Turgenevskaya and Tamga groups [10]. All the above-mentioned lithologic varieties of rocks from the Ruzhino cross-section were analyzed for Au and Pt by the methods of inductively coupled plasma atomic emission spectrometry (ICP AES) (at the analytical center of the Far East Geological Institute, FEB RAS) and glow discharge ion mass spectrometry (IMS) (at the Institute of Microelectronics and High Purity Materials RAS, the city of Chernogolovka) to define the prospective potential of the rocks for noble metal mineralization. The last method (IMS) is usually used in microelectronics to analyze metals and their alloys in a solid state. In this research the IMS was applied to non-conductive geological samples for the first time. It became possible due to the recently developed design of an ion source of glow charge using a hollow cathode [9]. An example of the obtained metal isotope spectra is shown on the figure where one can see the presence of $^{194, 195, 196}$Pt, $^{191, 193}$Ir, ^{192}Os, and ^{197}Au stable isotopes in the relative amount identical to their natural distribution.

To elucidate a possible association of Au-Pt mineralization with processes of graphitization, subsequent to analysing the samples by ISM and ICP AES, the same samples were fractionated in aqua regia and HF on solute and graphite in insoluble residue. The solutions including soluble silicate components and ore minerals were then analyzed using the AA-6200 spectrophotometer, which determined rather low Au concentrations (in the order of 10^{-5}–10^{-6} %) and the absence of platinum. Comparison of these data with Au and Pt contents in the total bulk of the samples shown on table permits the suggestion that there is an association of Pt and most of the Au with graphite. Evidently, only visible gold dissolves, while platinum and most of the gold remain in graphite. These data confirm the idea about an interplanal position of metals in graphite structure, being directly connected with carbon atoms [1]. It explains well-known problems with analysis and detection of platinoids in carbon-bearing rocks.

The conclusion is also supported by the results of experimental modeling of Au and Pt chemosorption on bitumoides at 200–500°C, 1 kbr [7, 8]. The experimental study had revealed high sorption capacity of graphite at 500^{o}C and 1 kbr: for Au – to 0,01 mAu/kg and for Pt – to 0,005 mPt/kg. It was conditioned by metal concentrating in benzene structures in the course of their dehydration.



Gold and platinoid isotopes ($^{191,\,193}$Ir, ^{192}Os, $^{194,195,\,196}$Pt, and ^{197}Au) on the spectrum of sample 03-3.

Gold and platinum content in graphite-bearing rocks, ppm

Sample	Au	Pt	Analyzed by	Au*
02-3	13	4	IMS	0,15
02-3	30	–	ICP AES	0,15
03-1a	5	16	IMS	–
03-3	3	6,7	IMS	0,01
03-5	5	52	IMS	0,001

Au* – content in solutes (see in text) measured by AA-6200 (analyst T. T. Ivanova).

The carbon from all graphite-bearing varieties of the studied rocks has been analyzed for isotopes to answer questions about a source of carbon during graphitization of rocks of the Ussuriiskaya series. This analysis was carried out at the Analytical Center of the Far East Geological Institute, FEB RAS (analyst T.A. Velivetskaya) using the Finningan MAT–252 mass-spectrometer. The accuracy of the isotopic relation $\delta^{13}C/\ \delta\ ^{12}C$ ($^{13}C_{PDB,}$ ‰) measurements made up ±0,1‰. The measurements of this relation in all studied rocks produced rather uniform values, slightly ranging from –8,5 to –8,7 ‰. Such values are definitely characteristic of a mantle source of carbon [11], evolving as a part of gaseous phases. This conclusion is supported by the abundant development of graphite along the zones of jointing, dislocations, and deep-seated faults. The obtained IR-spectra revealed an absence of any organic complexes and amorphous carbon in the rocks, while graphite occurs in all metamorphic and igneous rocks of the region. It may be explained by a high grade of metamorphism of the rocks: the temperature defined by the phase correlation method ranges from 570°C to 620°C at pressure equal to 3–4 kb [6]. According to the experimental data, amorphous carbonic matter transfers to graphite at a temperature about 500°C at P_{fl} = 1 kb [8].

Thus, gold and platinum contents of economic interest were ascertained in the graphite-bearing rocks of the Khanka massif for the first time. The commercial noble metals content, as well as the terrestrial abundance of graphite-bearing rocks and their considerable vertical thickness (over 3000 m) allows us to expect a major deposit of noble metals in this region. It can be related to gold-platinum-bearing formation of black shales and metasomatites of potential economic interest [5]. As to their lithologic characteristics, the described formation corresponds to the Voronezh type of ore-formations including highly carbon-bearing plagiogneiss of the Oboyanskay series that contains 1,3–7,5 g/t of Au and 5,9 g/t of Pt [2]. The studied rocks occurred in the core of thermal dome and differ by the high carbon and very low sulphide contents, at least within the described cross-section. At the wing parts of the dome structure, the amount of volcanogenic-terrigenous-carbonate protolith increases noticeably, accompanied by secondary processes of sulphidization and carbonization. Possibly, it is connected with a decreasing depth of the erosion section. In that part, the structure may be potentially prospective for gold-platinoid mineralization of the Carlin type.

1. *Bel'skii N.L., Nebol'sina L.A., Oksenoid K.G.* et al. Samples decomposition for analysis of platinoides within carbon-bearing rocks// Jour. of Anal. Chem. 1997. Vol. 52. N 2. P. 150–153 (in Russian).
2. *Chernyshov N.M.* New type of gold-platinoid mineralization within stratificated black-shale formations // Vestnik of Voronezh Univ. Geol. Ser. 1996. N 1. P. 114–133 (in Russian).
3. *Mishkin M.A., Khanchuk A.I., Zguravlev D.Z., Lavrik C.I.* The first data on Sm-Nd systematic of metamorphic rocks of Khanka massif // Reports of RAS. 2000. Vol 37. N 6. P. 813–815 (in Russian).
4. *Khanchuk A.I., Ratkin V.V., Ryasantseva M.D.* Geology and deposits of Primor'ye. Vladivostok, 1995 (in Russian).
5. *Korobeinikov A.F.* Untraditional complex gold-platinoid deposits of folded belts. Novosibirsk, 1999 (in Russian).
6. *Perchuk L.L., Mishkin M.A.* et al. Thermodynamic regime of rock. metamorphism of Khanka massif // Esse of physico-chemical petrology. Moscow, 1980. N 9. P. 139–167.
7. *Plyusnina L.P., Kuz'mina T.V., Likhoidov G.G., Narnov G.A.* Experimental modeling of platinum sorption on organic matter // Applied Geochemistry. 2000. Vol. 15. P. 777–784.
8. *Plyusnina L.P., Kuz'mina T.V., Nekrasov I.Ya.* Experimental study of gold sorption on organic matter at 20–500°C // Experiment in Geosciences. 2000. Vol. 9. N 1. P. 68–69.
9. *Sikharulidze G.G.* Ion source of glow discharge. 2001. Patent RU2174676 C1.
10. *Solonenko V.P.* Geology of graphite deposits of Eastern Siberia and Far East. Moscow, 1951 (in Russian).
11. *Zhmodik S.M., Mironov A.G., Agafonov L.V.* et al. Carbonization of hyperbasites of Eastern Sauan and gold-palladium-platinum mineralization // Geology and Geophysics. 2004. Vol. 5. N 2. P. 228–243 (in Russian).

БЛАГОРОДНІ МЕТАЛИ У ВУГЛЕЦЬВМІСНИХ ПОРОДАХ ПРИМОР'Я

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Досліджували Ханкайський кристалічний масив (Примор'я) для з'ясування вмісту золота і платини у графітоносних породах. Хімічні аналізи лейкократових гранітогнейсів, габро-амфіболітів, біотит-польовошпат-графітових сланців, які зазнали регіональної графітизації, засвідчили високий вміст у них вуглецю (до 29–36 мас. %). У всіх перелічених різновидах порід виявлено промисловий вміст золота (3–30 г/т) і платини (4–52 г/т). Ізотопний склад вуглецю (за вісьмома пробами) виявився незвично однаковим ($^{13}C_{PDB}$ = (–8,5)–(–8,7) ‰), що свідчить про мантійне джерело вуглецю. Отримані дані дають змогу корелювати золото-платиноїдну мінералізацію з регіональною графітизацією, виявленою у середньорифейських метаморфічних комплексах межиріччя Кабарги, Тамги і Кедровки.

Ключові слова: метаморфізм, платиноїди, золото, графіт, чорні сланці, Примор'я.

Стаття надійшла до редколегії 27.07.2005
Прийнята до друку 06.09.2005