



# Noble metal and graphite formation in metamorphic rocks of the Khanka terrane, Far East Russia



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## ABSTRACT

Noble metal–graphite mineralization has been identified in the Riphean–Cambrian metamorphic complexes of the northern Khanka terrane, Russia. The graphite mineralization is hosted in magmatic and sedimentary rocks metamorphosed under greenschist to granulite facies conditions. This paper provides the results of our study of the Turgenevo–Tamga graphite deposits. This study analyzes the geochemistry of the noble metals with the aim of determining the spatial relationships between noble metals and graphite. The graphitized rocks, analyzed by various geochemical methods, show a wide range of noble metal concentrations (ppm): Pt (0.02–62.13), Au (0.02–26), Ag (0.56–4.41), Pd (0.003–5.67), Ru (0.007–0.2), Rh (0.001–0.74), Ir (0.002–0.55), and Os (0.011–0.09). Crystallization from gas–condensates is indicated by the relationships between the noble metal mineralization and the graphite, and in particular the inhomogeneous distribution of graphite in the rocks, the inhomogeneous distribution of metals in the graphite, the microglobular graphite structures, and the carbon isotopic compositions. Thermal analysis and Raman spectroscopy indicate that some of the graphite formed from the metamorphism of sedimentary biogenic carbonaceous matter. The uneven distribution of noble metals in the rocks, and the compositional variability of the mineralization, implies that the origin of the metals was largely related to endogenic processes involving reduced fluids derived from depth. Our conclusion is that the noble metals and graphite mainly originated from magmatic fluids, but that some material was derived from exogenic and metamorphic sources.

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## 1. Introduction

The importance of fluid transport for the crystallization of metamorphic minerals has been recognized for many years (Korzhinskii, 1965; Ferry, 1996). The degree of volatile transport in carbonaceous complexes has been debated for many years, and it remains a problematic issue (Ferry, 1996; Manning, 2004; Galvez et al., 2013). Carbonaceous meta–terigenous sequences may contain economic deposits of gold, as for example in the large gold deposits of Muruntau in central Uzbekistan, Bakurchik, eastern Kazakhstan, Kumtor, Kyrgyzstan, Sukhoi Log, and the Patom Highlands, Russia (Yermolaev, 1995). These stratiform deposits consist of black shales that contain amorphous carbonaceous

matter of organic origin, but the possible enrichment of the rocks with endogenic carbon has been actively discussed (Vinokurov et al., 1997; Laverov et al., 2000). Fluid-driven deposition of graphite from cooling C–O–H fluids that permeated the lithosphere (along fractures) has been reported from the Stillwater complex, South Africa, the Borrowdale graphite deposit in the United Kingdom (Ortega et al., 2010), and the New Hampshire graphite deposits (Rumble et al., 1986). The ability of reduced carbon-bearing fluids from deep endogenic sources to accumulate and transfer metals is well established, and noble metal mineralization is well known in carbon-bearing sedimentary and magmatic rocks metamorphosed under the amphibolite and greenschist facies (Volborth and Housley, 1984; Ballhaus and Stampfl, 1985; Melcher et al., 1997; Distler et al., 2004; Wright et al., 2010). However, the nature of the fluid–rock interactions, as well as the mechanisms of graphite formation under relatively low-temperature conditions (especially  $T < 500$  °C), remain unknown (Chamberlain, 1967).

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Carbon is considered to play a significant role in ore-forming processes, particularly during the transport of noble metals in C–O–H–Cl ± F ± S-fluids (Ballhaus and Stampfl, 1985; Mogessie et al., 1991; Boudreau and McCallum, 1992). The participation of endogenic carbon during ore formation has been supported by the discovery of a new type of noble-metal mineralization in the Riphean–Cambrian metamorphic complexes of the northern Khanka terrane of Russian Primorye (Khanchuk et al., 2004, 2010). The graphitization here is of regional extent and affects rocks that have undergone greenschist to granulite-facies metamorphism, including schists, gneisses, granite gneisses, marbles, phyllites, and lamprophyre dikes. The graphitization is quite unlike the mineralization found in typical stratiform black-shales. In the Khanka terrane, exploration for graphite took place prior to 1950, particularly in the large deposits at Tamga (400 km<sup>2</sup>) and Turgenevo (225 km<sup>2</sup>) in the Lesozavodsk district of Primorye. Previous studies of these two deposits indicate a close association between the noble metal mineralization and the graphite. The aim of this study is to analyze the geochemistry of the noble metals, to determine the spatial relationships between noble metals and graphite, and to determine the sources of the carbon and the noble metals.

## 2. Geological setting

The graphite deposits of Turgenevo–Tamga are situated within the Khanka terrane, which is considered to be a Caledonian tectonic unit in the eastern continuation of the Central Asian Orogenic Belt. In the late Precambrian (730 Ma, according to the Sm–Nd method), the terrane underwent amphibolite and epidote–amphibolite facies regional metamorphism, and later, at the Cambrian–Ordovician boundary, greenschist to granulite facies metamorphism (Khanchuk et al., 2013). The granulites and amphibolites occur in the cores of narrow, tightly compressed folds, the axes of which mainly trend E–W, but with a few trending NW–SE and NE–SW. These rocks are cut by numerous faults of varying strike, and they are enveloped by a dome-like structure. Gabbroic and granitic intrusions of middle Paleozoic–Mesozoic age encircle the dome structure and occupy its center, whereas early Paleozoic granites seem to be distributed independently of the structure (Fig. 1).

The Turgenevo graphite deposit is situated in the Ruzhino metamorphic dome which contains amphibolite facies rocks of the Ussuri Group in its core. The complex is composed of garnet–biotite–feldspar and biotite–quartz–feldspar schists that are intercalated with marbles and conformable injections of biotite-rich and leucocratic granite gneiss. The schists are composed mainly of mafic minerals with a predominance (up to 40%) of biotite. Lens-shaped marble bodies, 10–75 m thick, were metamorphosed to skarns along the contacts with the granite gneiss, and they consist of calcite, zoisite, diopside, plagioclase, and K-feldspar. From the contact outwards, the skarns pass into diopside–calcite rocks, and then into marble. Thin (up to 1 m) lamprophyre and amphibolite dikes, conformable to the foliation of the country-rock schists, are enriched in TiO<sub>2</sub> and K<sub>2</sub>O, and contain 0.6–30% graphite. Green-schist-facies carbonaceous rocks of the Mitrofanovka Formation outcrop along the southern edge of the Ruzhino dome (Fig. 1). The rocks are similar in appearance to black shales, and contain fine-grained quartz (60–80%), sericite, and graphite (up to 12%), and some chlorite. Weakly metamorphosed phyllites and metasilstones of the Kabarga Formation overlie the Mitrofanovka rocks, and are cut by metadolerite dikes. The chemical compositions of selected graphite-bearing rocks are listed in Table 1.

The Tamga deposit is hosted by a carbonate-gneiss that includes graphite-gneiss with economic coarse-flaky graphite that is suitable for crucibles. Numerous lenses of skarn and graphitized marble are incorporated within the gneiss. The grade of metamorphic

alteration would suggest the rocks of the Tamga graphite deposit are related to the Ussuri Group.

## 3. Research methods

The determination of noble-metal concentrations in graphite-bearing rocks is problematic because graphite is inert to almost all chemicals. The quantitative physicochemical methods used in this study include atomic emission spectrometry (AES), inductively coupled plasma-mass spectrometry (ICP-MS), and atomic absorption spectrophotometry by thermoelectric atomization with prior extract concentration (AAS-TEA), all of which have been previously used by other workers to analyze noble metals in carbonaceous terrigenous rocks (Kucha, 1981; Mitkin et al., 2000). To determine the concentrations of Pt and Au in the graphite-bearing rocks from the Khanka terrane, we mostly used AAS-TEA with a sensitivity of 10<sup>−8</sup> wt%. Chemical decomposition was performed as follows. The samples were successively dissolved in mixtures of concentrated acids in the proportions HF:HNO<sub>3</sub> = 2:1, → HCl:HNO<sub>3</sub> = 3:1, → HCl. Next, the insoluble graphite residue was filtered and dissolved in HClO<sub>4</sub>, and both solutions were combined and converted into 2N HCl. Finally, noble metals were extracted with alkyaniline, and concentrations were determined by AAS-TEA on a Shimadzu AA-6800 spectrophotometer. The AAS-TEA method provides more reproducible results compared with other techniques, but is time consuming. The results obtained by AAS analysis for Au, Pt, and Pd concentrations in soluble silicate fractions and in the graphite residue are listed in Table 2.

Some of the graphite-bearing samples were analyzed after preliminary decomposition by fluoroxidation (Table 3). This method was first developed for black shales (Mitkin et al., 2000) and then adapted for the analysis of graphitized rocks (Mitkin et al., 2009). The technique involves the fluoridation of samples with BrF<sub>3</sub> and KBrF<sub>4</sub>, and after this, the fluorides are converted into chlorides and then analyzed by AAS or AES. High Au and Pt contents were first discovered in the graphite-bearing rocks of the Khanka terrane by ion mass spectrometry (IMS) analyses in 2004 performed by scientists of the Institute of Microelectronics and High-Purity Compounds, Russian Academy of Sciences, Chernogolovka. This method of analysis has an advantage in that it allows the high-sensitive detection of elements and noble metals in solid samples, and it does not require the preliminary dissolution of samples in strongly oxidizing reactants. The IMS analyses were conducted using an Element 2 ICP mass spectrometer manufactured by Thermo Electron Corporation. The spectrometer was equipped with a glow-discharge ion source based on a hollow cathode installed instead of an ICP-source sampler (Sikharulidze, 2004, 2009). Application of a new source of ions allowed us to analyze solid, non-conducting powder samples, and the high sensitivity of the method made it possible to analyze the powdered carbonaceous rock samples without pre-concentration of the metals. In addition, IMS allows the imaging of spectra for a wide range of metals and their isotopes. In earlier methods of analysis, the dissolution of samples at high temperatures often led to a drop in the detected values of the metals due to the emission of some carbon–metallic volatile complexes; the IMS method avoids this problem. The value of the IMS method is supported by comparisons of analytical results produced by both the AAS and IMS methods for the same samples (Table 4). Carbon isotope measurements were made using a Finnigan MAT-252 mass spectrometer at the Analytical Center of the Far East Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (FEGI FEB RAS), Vladivostok, Russia. Carbon isotope compositions in the graphite-bearing rocks of the Ussuri and Mitrofanovka formations are listed in Table 5.

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