Isotopic-Geochemical Features of the Generating of the Precious Metal Formations of the Jiamusi-Khanka Graphite-Bearing Province

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Abstract. Numerous occurrences of the precious metal mineralization located solely in the Jiamusi-Khanka province were detected within a single zone of the regional graphitization with ten kilometers submeridional strike towards the adjacent territories of the Primorsky krai (Russia) and the Heilongjian province (China), all the above said findings being obtained with the participation of the authors of the present scientific article. There are features of Dalnerechensk group (with Filinskoye being the largest of them), deposits of of Lesozavodsk group (Tamga, Turgenevo) and graphite-ore giant of Liumao Mashan group of the Heilongjian province in the Northern, central and Southern sides of this province respectively. The results of the isotopic-geochemical study of the graphite, the sulfides and the carbonates of these deposits, the formation of which has a common history with the one of the precious metal mineralization, indicate the participation of deep derivated recomposed fluids and the light isotopic-biogenic matter of the host rocks in the ore formation. Besides, the carbon and the oxygen from at least two more isotopic-contrast sources intruded into the ore-forming system. Some minerals were formed under the influence of the intrusive acidic melts on the carbonate rocks, other one were generated due to the involvement of the meteoric waters in the ore formation.

1. Introduction
The majority of high technologies which are indicators of the level of development of the industrial production in the advanced countries are inconceivable without graphite use. Unique properties of this mineral together with the latest discoveries in the field of nuclear power, electronics and nanotechnologies have completely changed our vision of opportunities of its usage [1]. Low-ash crystal graphite is widely applied in the various fields of industries. Graphite serves as an additive for increasing the fireproof properties of materials in metallurgy. Thanks to its high conductivity, plasticity and mechanical strength graphite is widely used for producing galvanic cells, electrodes, alkaline accumulators, etc in electrical engineering. High-quality graphite is used as a moderator of nuclear reactions in atomic reactors, it’s also applied in jet propulsion (rocketry) for producing bladed turbines and rockets, the colloidal graphite, oxidized and thermal expanded graphite [2]. Graphite is included in the list of critical minerals in the countries of the European Union and China. The main deposits of high-quality crystal graphite are located in China, India, Brazil, the Czech Republic, Canada and Mexico. At the same time, the main producer and exporter of graphite raw materials is
China. Few Russian enterprises specializing in extraction of graphite provide rather insignificant supply of graphite for our country. Most of the crystal graphite is imported from abroad.

The graphite-bearing rocks are deposited along vast territories within the Far East of Russia and the North-East of China. Just in the Primorsky Territory alone they form a wide zone elongated into the submeridional direction for many tens of kilometers along the border of the Khanka and Jiamusi terrain from the city of Dalnerechensk in the North through the city of Lesozavodsk to the city of Jixi (the Heilongjiang Province, China). The early stage regional metamorphism of the low-gradient wide-zonal type was established within the zone under the conditions of amphibolite and epidote-amphibolite facies, the first one being equal to 730 million years. The late stage of metamorphism including facies from granulites to green schists is associated with the collision events at boundary between the cambrian – ordovician. One of the most important results of geological studies conducted within this zone during recent decades is the discovery [3] occurrences of the precious metal mineralization. Five deposits were found in its Northern Russian part called the Dalnerechensk field (with Filinskoye being the largest of them), there are over thirty deposit (including the well-known Tamga and Turgenevo graphite deposits) in the center (the Lesozavodsk field); and about forty deposits are located in the Southern Chinese In the segment (the Mashan field), including the graphite ore giant Lumao, where more than half of the world crystalline graphite is produced [4, 5, 6]. Taking into account the wide area of the occurrence occurrence of metalliferous graphitized rocks with their significant vertical thickness being equal up to up to 3000 m, we can assume that, in addition to producing graphite, they accumulate significant resources of precious metals (PM). The mentioned graphite-bearing areas were proposed to be combined into single Jiamusi-Khanka province [7]. The determination of the ore matter source of the studied deposits is among the key problems of the geology. The isotopic composition of graphite, sulfide and carbonate minerals, bearing the important genetic information on the origin and conditions of the formation of precious metal’s mineralization was studied for solving this problem. The sampling was carried out from quarries and core of drill holes, outcrops of host rocks and ore formations of the most of the currently known deposits of the Dalnerechensk, Lesozavodsk and Mashan graphite bearing area.

2. Methodology of experiment
The isotopic analysis of carbon in graphitized rocks was carried out on the Finnigan MAT 253 isotope mass spectrometer applying the dual inlet system. The samples were prepared for the mass spectrometric isotopic analysis of carbon by the method of carbon oxidation in the CuO oxidation column [8]. The analyzed sample is mixed with a powder of copper oxide, which is previously calcined at the temperature of 900°C in the atmosphere for 30 minutes. The mixture is placed in the quartz reactor, then the reaction column is loaded, and the sorbed gases and water vapors are removed by means of pumping out of ≤10-3 mm Hg (VHM) of the substance. Carbon oxidation is carried out in vacuum conditions at the temperature of 850°C. Conversion efficiency is provided by the CuO column preheated to 850°C. The reaction products are frozen into the trap at the temperature of -196°C and cryogenic purification of CO2 is performed. The reproducibility of the method is ≤0.1%o.

The isotopic analysis of sulfur sulfides was performed according to the method of V.A. Grinenko [9]. Sulfide sulfur is oxidized to SO2 using copper oxide as an oxidizing agent. The oxidation reaction is carried out in vacuum conditions at the temperature of 900°C. The derived SO2 is purified of the remaining reaction products at temperature-controlled cryogenic trap. Purified SO2 is frozen in a separate ampulla for measuring δ34S. Sulfur isotopic ratios were measured on the FinniganMAT 253 isotope mass spectrometer (ThermoFinnigan, Bremen, Germany) using a dual inlet system. Measurements of the isotopic composition were carried out in accordance with the laboratory working standard, the calibration of which was performed using the international standards IAEA-S-1, IAEA-S-2, IAEA-S-3 and NBS-123. The weight of the analyzed samples is equal to 10 mg. The ratio error in determining δ34S (1σ) is equal to 0.1%o, n = 5.

The isotopic analysis of oxygen and carbon of the carbonates was carried out using both the high vacuum system for the decomposition of carbonates in the phosphoric acid [10] and the MAT isotope
mass spectrometer (Fisher Scientific, Germany). The weight of the analyzed samples was approximately 5 mg. Measurements of the isotopic composition were carried out in comparison with the laboratory standard, the calibration of which was performed using the international standards NBS-18, NBS-19 and IAEA-CO-8. The results of measurements of $\delta^{18}$O and $\delta^{13}$C are presented in the generally accepted form

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \, (\%_0),$$

where $R_{\text{sample}}$ and $R_{\text{standard}}$ are the ratios of $^{18}$O/$^{16}$O or $^{12}$C/$^{13}$C in the sample and standard, respectively. The measurement results of $\delta^{18}$O and $\delta^{13}$C are given in accordance with the international standards VSMOW and VPDB, respectively. The ratio error in determining the $\delta^{18}$O and $\delta^{13}$C (1σ) values was 0.05%0 for the laboratory standard and 0.1%0 for samples.

3. Results of experiment and their discussion

The graphite, or to be more exact, the isotopic composition of its carbon which is a kind of a “visiting card” of the Jiamusi-Khanka province can be the key to deciphering the nature of the ore substance. The formation of graphite in nature, as it has been noted earlier [11], is possible due to metamorphism of organic matter, the effect of magmatic intrusions on carbonate rocks, and formation of the ore substance saturated with CH$_4$, CO, and CO$_2$ from the deep fluids. Since these sources are characterized by different values of the $^{13}$C/$^{12}$C isotopic ratios, these parameters can be considered indicators of the genesis of the graphite. Thus, the carbon isotopic characteristics of the organic matter vary in the range of $\delta^{13}$C from -17 to +40%0 with average values equal to 26...-28%0 [12]. The isotopic-carbon weight of the marine carbonates ($\delta^{13}$C from -2 to +2%0) and the mantle carbon (from -5 to -7%0) are significantly heavier than the one of the organic matter [13]. In our case, all these sources of graphite are combined within the Jiamusi-Khanka province, which somewhat complicates the interpretation of the obtained isotopic information. The graphites from granite gneisses or schists are the most suitable specimen for determination of the sources of the ore substance, since in this case the influence of isotopic exchange with carbonate carbon can be avoided.

As our studies have shown, the graphites of Russian granite gneisses possess quite a high degree of homogeneity in the terms of isotopic composition and vary in the range from -2.1 to -8.8%0, which indicates a mantle source of the carbon. At the same time, the $\delta^{13}$C values of the graphite of the Filinskoye deposit (lower suite of the ore-bearing section) vary from -2.1 to -5.5%0, while the graphites of the Turgenevo deposit (the Western section), hosted in the rocks of the upper formation, are characterized by lower $\delta^{13}$C values (from -8.5 to -8.8%0). The graphite of Chinese granite gneisses appeared to be even lighter if to take into account its isotopic composition ($\delta^{13}$C reaches -11.5%0).

We observe the similar situation when comparing the isotopic compositions of graphites of Russian and Chinese schist. The range of $\delta^{13}$C changes occurring in the schist crushing zones of the Filinskoye deposit (lower suite of the ore-bearing section) vary from -11.1 to -11.5%0. The graphites from the schists of the Turgenevo deposit (the Western section) appeared to contain carbon with a lighter isotopic composition with $\delta^{13}$C ranging from -19.3 to -23.6%0. The similar values of $\delta^{13}$C are also characteristic for the graphites from the Lumao schist (up to -23.5%0).

As follows from the obtained data on the isotopic composition of sulfur of sulfides of Russian and Chinese deposits, sulfides having similar isotopic characteristics are found out to be associated with isotope-heavy graphites. The highest values of $\delta^{34}$S (up to +2.0%0) are typical for the ores of the Lumao deposits. These parameters are reduced to -2.0%0 for sulfur sulfides from deposits of the Dalnerechensk and Lesozavodsk fields. The proximity of the range of variations in the $\delta^{34}$S values of these minerals to the “meteorite” sulfur level testifies in favor of a deep source of ore matter. The sulfur of sedimentary-diagenetic origin plays the main role in the sulfide mineralization of the graphite schist. The range of fluctuations of $\delta^{34}$S pyrites of Russian and Chinese objects is rather narrow (from -11.0 to -13.0%0), taking into consideration the presence of the biogenic pyrite in the rocks.
Two trends of the evolution of the ratios oxygen and carbon of carbonate minerals (figure) are clearly observed on the diagram below. One of them corresponds to the transformation trend of marine carbonate rocks at an early stage of the ore-forming process.

Figure 1. The nature of the ratios of the isotopic composition of oxygen and carbon in carbonates of the ore formations of the Jiamusi-Khanka province. Fields: 1 - Filinskoye (scarns); 2,3 - Height 316 (2 - scarns, 3 - post-ore calcite); 4,5 – Turgenevo (4 - scarns, 5 -graphite ore); 6,7 - Tamga (6 - scarns, 7 graphite ore); 8, 9 - Ruzhino (8 – marble, 9 - scarns); 10, 11, Lumao (10 - graphite ore, 11 - marble). Field of mantle carbonate rock compositions according to [20].

Thus, the $\delta^{18}O$ and $\delta^{13}C$ values of marbles vary in the range of 22.2–25.4 $\%_0$ and $-0.7–3.6 \%_0$ respectively, which is characteristic for the deposits of metamorphic origin [14]. The isotopic compositions of oxygen and carbon are distanced from marbles in scarns, shifting to the side of lighter values from 16.2 to 20.3 $\%_0$ and from -1.2 to 2.0 $\%_0$. The enrichment of scarns with light oxygen and carbon has been described in scientific literature many times.[15,16] It’s connected with the metamorphic recrystallization of the rocks addition of isotopic light solutions into the last ones, the processes of the high-temperature decomposing of the carbonates accompanied by the kinetic effects of isotope fractionation. The oxygen-isotopic composition of carbonates of ore veins (9.0-10.0 $\%_0$) is even more lighter, which indicates the appearance of light meteoric waters in the system. The involvement of the last ones in the formation of scarns as it has been mentioned earlier [17, 18, 19] causes the high degree of decrease of oxygen weight of the matters mentioned in the previous sentence. The polygenicity of carbon and oxygen sources caused a wide dispersion of $\delta^{18}O$ and $\delta^{13}C$ values of carbonate rocks.

Another trend recorded a decrease in the isotopic composition of the calcites of the graphite veins in the direction from the Turgenevo and Tamga deposits to Lumao ones. The field of values of the first
of them coincides with the contours of the mantle source [20]. The calcites of the Tamga deposit are depleted by the heavy C isotopes to a lesser extent, changing from -8.5 to -10.0 %0, respectively. The degree of lightness of the isotopic composition C reaches its maximum value in Lumao calcite (from -11.5 to -12.0 %0). The borrowing of the biogenic matter by the mantle fluids in the process of ore formation from the host rocks must have been the most probable reason for the occurrence of light carbon. At the same time, if we compare the isotopic parameters of ore carbonates (figure) of Lumao with those of the Tamga and Turgenevo deposits we can conclude that there was the consequent enrichment of the first ones with heavy oxygen isotopes. This isotopic shift must have occurred due to the ingress of heavy oxygen into the system caused by the high-temperature decomposition of carbonate rocks in the process of the metamorphic recrystallization of the last ones.

4. Conclusion
Summarizing the above mentioned information, we’d like to mention that the obtained data on the isotope of carbon, oxygen, and sulfur of the minerals of the Russian and Chinese deposits allow to suggest that at least two isotopic-contrast sources influenced the formation of the province's syngenetic ore mineralization namely: mantle fluids and sedimentary rocks with organic compounds. The wide range of the changes in the isotopic compositions of carbon, oxygen, and sulfur of the studied objects indicates that biogenic carbon influenced the first ones in different ways. In any case, the deep fluid flows were the main suppliers of ore matter in the formation of graphite-bearing ores of the Jiamusi-Khanka province. In addition, carbon and oxygen invaded into the ore-forming system from at least two other isotope-contrast sources. Some minerals were formed under the influence of intruded acidic melts into carbonate rocks, others - due to the involvement of meteoric waters into the ore formation.

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