The Distribution of Noble Metals in Metasomatites of the Kirchenovskoye Deposit (Transbaikalia)

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Abstract. The Kirchenovskoye gold-silver deposit is one of the fairly large deposits in the Olovyaninsky region. In addition to rich ore mineralization, the distribution of noble metals in the host rocks is of interest. For five selected rocks, the contents of noble metals (Rh, Pd, Ag, Pt, Au) were determined, the main part of which is represented by metasomatites: beresitized granite, graphite metasomatite (gneiss), graphite shale, mudstone and rocks from the weathering crust. For this, the method of mass spectrometry with inductively coupled plasma (ICP MS) was used. Promising mineralization for Au, Ag, and Pd (mudstone, graphite shales and gneisses) have been identified. The concentration of noble metals in ores and host rocks occurred due to the removal of these metals from the granitoid massif by hydrothermal solutions.

1. Introduction
Currently, the active reserves of alluvial and ore gold are decreasing due to the gradual use of the mineral resource base favorable for the development, deterioration of the mining-geological and mining-technical conditions of exploitation of deposits, a decrease in the natural content of noble metal in the extracted raw materials [1, 2]. In this case, technogenic waste and host rocks can be considered as an important component of the mineral resource base. Moreover, the latter are often the first. Such raw materials are approved by reducing capital and operating unit costs for its processing [2].

Interesting in this regard is the Kirchenovskoye gold-silver deposit. It contains rich noble metal mineralization both in the ores and in the host rocks. The deposit is located on the right coast of the Turga river, 6 km north-east of the Calangui village. The site is part of the Turgin ore cluster, Kukulbeysky ore district. The deposit is confined to a complex zone of silicification, propylitization and beresitization in the exocontact of the Shakhtama granitoids. The ores belong to the gold-silver poor-sulfide industrial type with the separation of two varieties: oxidized and primary. Ores are confined to quartz veins. Gold content 1.5-2.0 g / t, silver content up to 85 g / t. The ores of the deposit, as well as the adjacent mudstones with a high content of sulfide minerals in them, are well studied [3]. However, the question of the distribution of noble metals over the host rocks remains open. This question is relevant both in identifying potential noble metal mineralization, and in identifying features for a specific type of deposit.
The purpose of the study is to study the distribution of noble metals in the metasomatically altered host rocks of the Kirchenovskoye deposit and to establish the reasons for this distribution.

2. Materials and methods
The material is represented by five rocks that underwent metasomatic transformations: beresitized granite, quartz veinlets from this rock, mudstone, graphite-bearing plagioclase-sericite-quartz metasomatite, graphite-quartz-sericite shale, crushed stone from the weathering crust. All rocks are in contact and near-contact zones with ore quartz veins. Beresitized granite is represented by a dark gray rock with a green tint, micro-grained structure and slightly shale texture. Mineral composition of the rock is following (wt%): 50 quartz, 25 carbonate, 15 chloride, 10 sericite, less than 1 for a microcline with biotite. Noted of disseminated ore mineralization is represented by pyrite. The rock is dissected by quartz veins up to 1 cm thick, containing inclusions of pyrite and galena. Mudstone has a gray color with a blue tint, its texture is shale. The rock contains a fairly high amount of sulfide minerals (about 5 wt.%). The rock forms a layer up to 0.5 m thick near ore-bearing quartz veins and belongs to the Lower Jurassic Tamenga Formation (J1tm). The mineral composition of mudstone is following (wt%): 53 muscovite, 32 quartz, 10 clinochlore, 2.8 pyrite, 1.0 arsenopyrite, 0.5 covellite, 0.5 freibergite, 0.2 argentite and galena. Graphite-bearing plagioclase-sericite-quartz metasomatite (further - graphite gneiss) is a yellowish-gray rock with a micro-grained structure and gneiss-like texture. Mineral composition is (wt%): 55 quartz, 30 sericite, 10 plagioclase, 5 graphite and sulfides. Graphite forms thin plates up to 0.1 mm thick. In structure and composition, the metasomatite is close to gneiss. Graphite-quartz-sericite shale (further - graphite shale) is a dark gray shale-textured rock, consisting of (in wt%): 35 quartz, 35 sericite, 5 plagioclase, 25 graphite and sulfides. Crushed stone from the oxidation zone is a rock of psephite and psammitic fractions of an ochre-yellow color with quartz, sericite, chlorite and plagioclase predominant in the mineral composition.

The samples were studied using a Carl Zeiss Axio Image optical microscope and a Tescan Vega 3 scanning electron microscope. The impurity composition, including the content of noble metals, was determined using an ELAN 9000 inductively coupled plasma quadrupole mass spectrometer (further - ICP MS) in accordance with the methodology [4]. The analysis was carried out at the Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences; its accuracy is 0.01-1 ppm.

3. Results and discussions
Based on the ICP MS analysis and examination of the samples under an optical microscope, rich sulfide mineralization was established directly in the ores - quartz veins of beresitized granite and in mudstones for both noble and nonferrous metals. The main identified ore minerals are pyrite, arsenopyrite, chalcopyrite, covellite, galena, sphalerite, freibergite, and argentite. Secondary ore minerals are represented by scorodite, aglesite, matsapelite, and carminite. Gold in ores forms both native precipitates and is present as a chemically bound impurity in sulfides (chalcopyrite, pyrite). Silver is in mineral form (freibergite and argentite) and in the form of impurities in galena. The poorest rocks in terms of the variety and quantity of ore minerals are graphite gneiss and shale. They contain low noble metals (except for palladium). The form of occurrence for other metals has not been established. In general, five precious metals have been identified in the studied rocks: Au, Ag, Pd, Rh, Pt. Chemical analysis data are shown in Table 1.
Table 1. The content of precious metals in the studied metasomatites and altered rocks, g/t.

|                | Beresitized Granite | Quartz veins of beresite | Mudstone | Graphite metasomatite | Graphite shale | Weathering crust |
|----------------|---------------------|--------------------------|----------|----------------------|---------------|-----------------|
| Au             | 0.04                | 2.19                     | 5.83     | 0.01                 | 0.06          | 1.11            |
| Ag             | 38.39               | 608.05                   | 686.13   | 10.37                | 9.99          | 32.90           |
| Pd             | 2.65                | n/f                      | 2.36     | 3.66                 | 6.41          | 0.99            |
| Rh             | 0.00                | 0.05                     | 0.16     | 0.01                 | 0.00          | 0.01            |
| Pt             | n/f                 | n/f                      | n/f      | 0.01                 | 0.02          | n/f             |

3.1. Gold distribution

One of the two main components at the deposit. The main concentration of metal is observed in mudstone and the weathering crust - the content is higher than the standard (5.8 and 1.1 g / t, respectively). If the concentration in the weathering crust occurs due to the removal of some of the rock-forming minerals by wind and water flows, then the concentration of gold in mudstones is explained by the presence of the latter in the contact zone with the ore vein. The advantage is the presence of graphite in mudstones, which adsorbs noble metals on itself. In other rocks, gold grades are close to clarke values. In graphite shales and gneisses, an increase in gold content is observed with an increase in graphite content. However, the low metal content in these rocks is explained by their remoteness from the ore vein.

3.2. Distribution of platinum group metals

The presence of only three metals from this group was established in the rocks: Pd, Pt, Rh. High contents of palladium is up to 6.5 g / t. For the rest of the elements, this value is within the clarke content. It has been established that with an increase of the graphite content in the rocks, the palladium content increases (it reaches a maximum in graphite shale, where the graphite content is about 25%). In this case, graphite adsors a noble metal on itself. This is the reason for its high content in graphite gneiss and shale, mudstone (the presence of graphite in this rock is noted). The situation is similar for platinum and rhodium (the content of the latter is higher in graphite-bearing mudstone than in quartz cuttings). However, gold and silver were not concentrated in graphite metasomatites. This suggests that the formation of the main gold-silver ores and palladium-bearing rocks occurred at different stages of the deposit formation. The only "binder" rock containing all the studied noble metals (with the exception of Pt) is mudstone. This is due, presumably, to its location both near quartz veins and near graphite rocks.

Sources [5, 6] show that Pd and Pt in graphite shales (for example, the Soyuznoe deposit) are in a metallic form in the form of microdispersed isometric grains. The metal is located in flakes and graphite crystals. A similar form of finding is possible in the samples under study. However, despite the high content of palladium in the rocks, there are currently no cost-effective methods for extracting noble metal from such ores.

3.3. Silver distribution

The second main component to be mined for the deposit. Its distribution is the same as gold. But, the silver content is much higher than that of gold. Enormous Ag contents are found in ore veins and mudstone (up to 600-700 ppm). In other rocks, the content is 10-20 times lower, while it is higher than the standard grade. The lowest silver concentrations are found in graphite-bearing rocks (shale and gneiss). The noble metal forms two main minerals [3], and one of them - freibergite - is primary, formed together with the main ore, and the second - argentite - secondary, forms shells around ore minerals. The latter indicates that there may have been a repeated exposure of the ore to hydrothermal solutions. This could lead to a small concentration of metal in graphite-containing rocks.
3.4. *Genesis of metasomatic rocks*

The genesis of the studied rocks is analyzed in terms of the contents and relationships of rare-earth and rare metals.

The distribution graph of rare earth elements (Fig. 1) is characterized by a sharp slope of the curve towards heavy rare earth elements (HREE) and flattening in the region of the same elements ($\sum$REE = 16.4-110.66 ppm; La / Yb = 1.49-34.56). The graph for quartz veins is even, with virtually no deviations.

As can be seen in the graph, all samples, except for quartz veinlets, are characterized by a negative europium anomaly (0.15-0.35) at Eu <0.95. Depletion in europium indicates formation in the upper continental crust.

![Figure 1](image1.png)

**Figure 1.** The distribution diagram of rare-earth elements for the studied metasomatites (the contents are normalized to the contents in chondrites). Legend: Grph sh – graphite shale, Mud – mudstone, Weath cr - weathering crust, Grph gn - graphite gneiss, Ber gr – beresitized granite, Q vein - quartz veinlets from beresite.

This removed from the La / Th and Th / U ratios in graphite gneiss, beresitized granite, and graphite shale (Fig. 2), which indicates orthogneisses.

![Figure 2](image2.png)

**Figure 2.** Diagram of Th and U outflow from magmatic rocks.
According to the ratio of Rb-Y + Nb and Nb-Yb, beresitized granites are referred to as island-arc granites (Fig. 3).

![Figure 3. Genesis of granites in relation to the contents of Rb, Y, Nb. The yellow points on the diagrams are the studied beresitized granite.](image)

Based on the conclusions drawn from Fig. 1-3 and according to the literature data [7, 8], the source of noble metals (with the exception of palladium) is the plutonogenic massif, composed of Shakhtama granitoids (granite, diorite). This is also indicated by the very low gold and silver contents in the beresitized granites. Palladium is presumably associated with the late stage of the formation of the deposit, when already gold-silver ores were formed. Presumably, it was formed from secondary hydrothermal solutions differing in composition from the original ones (at which gold-silver ores were formed). But this variant indicates the form of occurrence of argentite (Ag₂S) in graphite-bearing mudstones: shells are minerals around sulfides and other silver minerals. Also, the option with metamorphic transformation of ores is not excluded, when palladium is distributed over graphite-bearing rocks due to changes in the thermodynamic parameters of the environment.

4. Conclusions

Thus, the contents of noble metals in the host ores of the metasomatically altered rocks of the Kirchenovskoe deposit have been established, and promising mineralization for Au, Ag, and Pd (mudstone, graphite shales and gneisses) have been identified. The concentration of noble metals in ores and host rocks occurred due to the removal of these metals from the granitoid massif by hydrothermal solutions.

An unclear picture remains with palladium, which was formed under different conditions. Two options are being considered: the concentration of palladium due to new hydrothermal solutions, which carried a precious metal, or due to the metamorphic transformation of already formed ores. Therefore, the question of the formation of palladium-rich graphite shales and gneisses remains open.

5. References

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Acknowledgments
The reported study was funded by RFBR according to the research projects № 19-38-90080 \19 and № 18-29-24081\19.