

## Noble Metals in Graphitized Rocks of the Khanka Terrain (Primorye): Evidence from Analytical Results Based on Decomposition by the Fluoroxidizing Method

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Development of the geology, geochemistry, and analytical chemistry of noble metals (NM) in the past 30 years has provided new insights into the nature of unconventional complex gold and platinum group metal (PGM) deposits. In particular, such deposits confined to black shales were discovered in Caledonides of the Central Asian orogenic belt, such as the well-known Muruntau, Kumtor, Zun-Kholba, Irokinda, Sukhoi Log, Nezhdaninskoe, Natalka, and others. In the past 10–15 years, commercial PGM concentrations were detected in ores of these deposits [1–4 and others]. The PGMs in these deposits are traditionally assigned to the carbonaceous matter (CM) of rocks. However, it turned out that they are likely (and primarily) associated with sulfides. Geochemical aspects of PGM concentration in rocks (and ores) and issues of their reliable determination have attracted the main attention in discussions devoted to the problem of PGM occurrence in black shales in the recent period of more than 20 years [4, 5, and others].

The Khankai massif is located at the center of the Central Asian orogenic belt in the Russian Far East. The NM mineralization (Au + PGM) was recently discovered in graphitized rocks [6] of the well-known graphite deposits in the Lesozavodsk region of Primorye [7]. Relative to the typical black shales mentioned above, these rocks are almost devoid of sulfides [8]. However, this interesting feature is provoked apparently by tech-

nical difficulties in the analysis of PGMs. For example, analysis of Au and Pt by glow discharge ion mass spectrometry (GDI MS) [9] yielded 3–30 and 4–52 g/t, respectively. Duplicate analysis of the same samples by atomic coupled plasma atomic emission spectrometry (ICP AES) and atomic absorption spectrometry by thermoelectric atomization with prior extract concentration (EC TEA) yielded, on average, two orders of lower Au concentrations, while the presence of Pt was not confirmed at all [10]. However, such contradictory results are common for the analysis of black shales due to both poor representativeness of the samples analyzed and losses of the NM during the chemical preparation of samples and their transfer to solutions, as was demonstrated for the Natalka deposit [5, 11, and others].

The present paper is aimed at scrutinization of the NM mineralization in graphitized metamorphic rocks of the Ruzhino ore occurrence. For this purpose, we chose specimens of rocks that were comprehensively investigated by various methods, including the new methods of sample preparation based on decomposition by fluorinate oxidation. Application of these methods provided the maximal disintegration of the refractory material in samples and the minimal loss of PMGs relative to black shales [11–13].

The NM-enclosing and CM-containing rocks were formed in the study region during the Middle Proterozoic–Lower Cambrian. They were metamorphosed in two stages (Fig. 1). The earlier (regional) low-gradient metamorphism, which took place approximately 730 Ma ago, was characterized by alteration of rocks under conditions varying from the epidote–amphibolite to the amphibolite facies. During the later (Cambrian–Ordovician) stage of metamorphism related to collision, the rocks were altered under conditions varying from the greenschist to the granulite facies.

We chose 21 specimens from the collection after the preliminary mineralogical description and typification of rocks. The specimens were crushed in a zirconium ball crusher, sieved up to –100 μm fraction, and quar-

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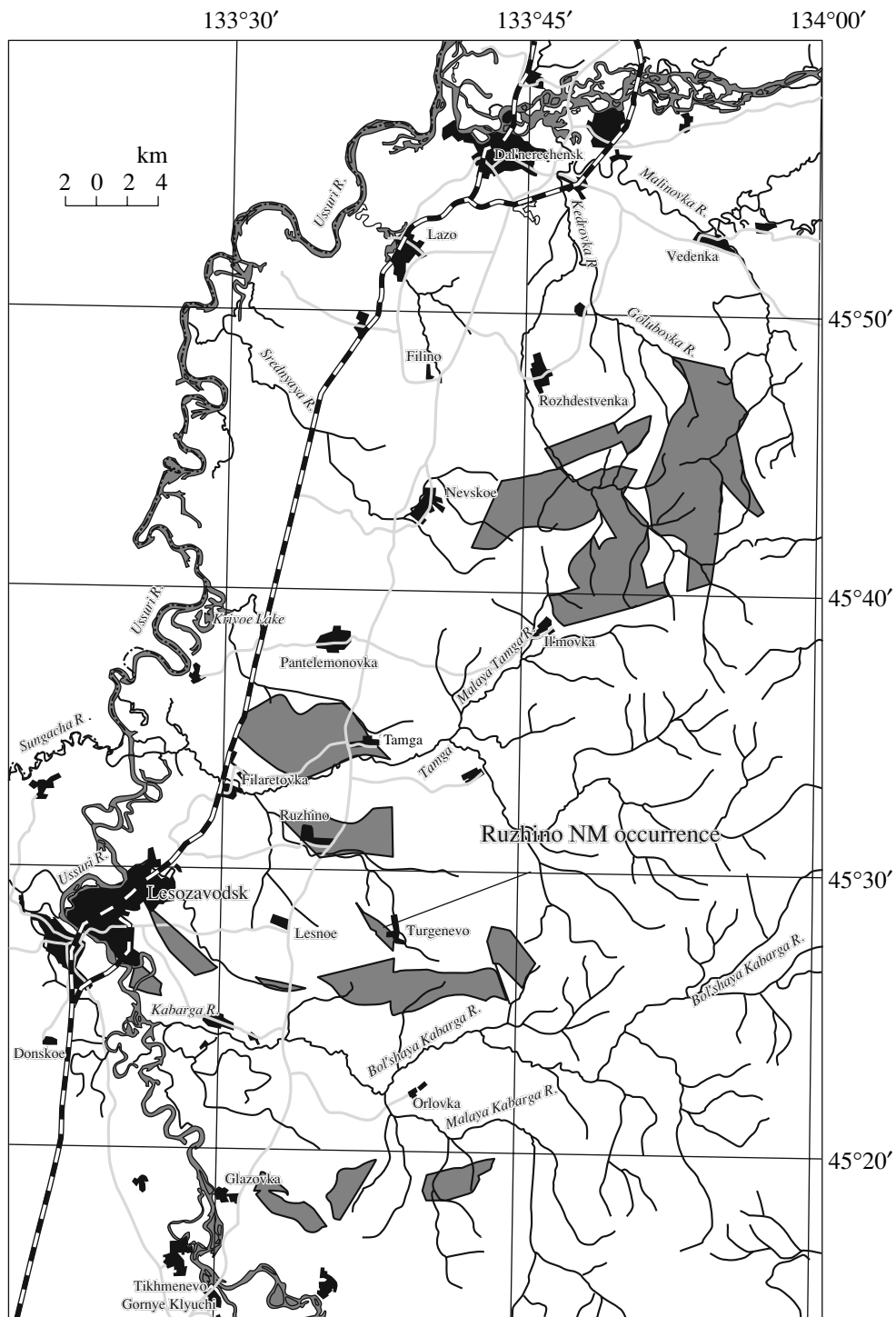


Fig. 1. Scheme of the distribution of graphitized (dark shading) rocks in the Khanka terrain.

tered. Then, their weighed portions (40–50 g) were pressured in polyethylene glasses. We studied mainly Riphean (regionally metamorphosed) rocks of the Turgenev Formation (see Table 1 for its composition).

The Proterozoic rock mass is intruded by both concordant and metamorphosed biotite and leucocratic

gneisses, as well as thin lamprophyre dikes. Almost all rock varieties include a certain amount of the CM (graphite in our case). Graphite (up to 40 vol %) is developed as dissemination, lenses, and quartz–graphite or graphite veins. The rocks also contain products of potassic metasomatism (veins and/or megacrysts of

**Table 1.** Graphitized rocks of the Ruzhino sector, wt %

Component	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	70.82	34.74	66.50	38.61	50.54	38.56	52.05	39.39
TiO <sub>2</sub>	0.22	0.19	0.05	0.02	1.65	0.32	1.11	0.39
Al <sub>2</sub> O <sub>3</sub>	12.61	12.03	12.33	20.19	20.51	8.95	20.27	8.88
FeO	0.26	5.50	0.16	0.64	7.90	0.85	6.50	0.78
Fe <sub>2</sub> O <sub>3</sub>	0.32	0.29	1.65	0.69	1.50	2.18	3.60	2.84
CaO	3.04	0.20	0.28	4.12	3.71	2.51	2.14	2.51
MgO	0.32	0.58	0.62	0.56	3.67	2.16	3.74	2.16
MnO	0.02	0.03	0.01	0.02	0.18	0.06	0.20	0.05
Na <sub>2</sub> O	0.95	0.93	1.90	2.18	4.07	1.83	3.13	1.72
K <sub>2</sub> O	7.90	3.03	6.38	2.92	3.85	1.58	5.67	1.51
H <sub>2</sub> O <sup>-</sup>	0.10	0.59	tr.	0.20	tr.	tr.	0.57	tr.
H <sub>2</sub> O <sup>+</sup>	0.98	3.73	2.45	2.16	2.02	5.97	0.29	4.58
C <sub>tot</sub>	2.08	36.47	7.33	27.41	<0.5	34.57	0.62	33.84
S <sub>tot</sub>	0.04	0.53	0.01	0.01	0.03	0.04	0.01	0.04
Total	99.66	98.64	99.67	99.73	99.63	99.58	99.90	98.62

Note: (1–3) Graphitized leucocratic granite gneisses; (4) graphitic metasomatite after biotite granite gneiss; (5, 7) biotite–feldspar schists; (6) granite–biotite–feldspar–graphite schist; (8) graphitized lamprophyre. (tr.) Traces. Analyses were performed in the Far East Geological Institute, Vladivostok (Zh.A. Shcheka, analyst).

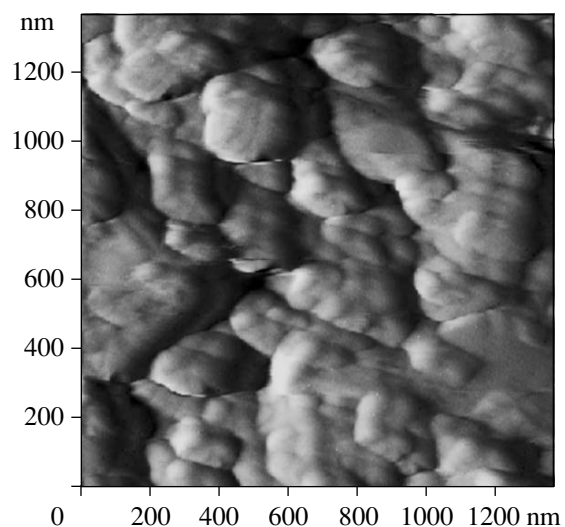
microcline and biotite). The cross-cutting character of the graphite veins and graphite-bearing quartz testifies to the redistribution of graphite by the superimposed processes during the formation of the productive sequence. The graphite distribution pattern in the rocks studied and their type differed basically from that in the CM of auriferous black shales in East Siberia and Northeast Russia reported in [1–3 and others]. In particular, the CM of rocks in the Ruzhino ore occurrence is not only graphitized completely, but also apparently devoid of sulfides. The results of electron microscopy show that particles of even weakly graphitized rock varieties have a fine and sufficiently compact graphite coating. Their photomicrograph clearly shows noncrystalline (“curdy”) aggregates (up to 100 nm across) in the obviously carbonaceous coating (Fig. 2).

We used a complex analytical method because of the absence of attested PGM standards with the corresponding matrix and required range of CM content (0.5–36.5 wt %). This method made it possible to compare the results of three independent schemes of sample preparation for the analysis in combination with various methods of NM determination (in powder and in solutions obtained by the decomposition of samples by fluorinate oxidation or their baking with niter). In some cases, we analyzed the absorbing solutions from the gaseous products of ignition.

**Scheme 1.** Samples (3–5 g) were fused together with potassium tetrafluorobromide (KBrF<sub>4</sub>), and the fluorides obtained were converted into chlorides according to the scheme described in [13]. After the prior concentration of CM from chloride solutions, its

concentration was determined by the EC TEA AAS method [14 and others]. We could determine Ag, Au, Pd, and Pt. The detection threshold was 0.3–3 ppb. Conversion of fluorides into chlorides was performed twice. Therefore, we had to analyze both the first (IR-1) and second (IR-2) insoluble residues left after the fluorinate decomposition.

**Scheme 2.** Samples (3–5 g) were fused together with KBrF<sub>4</sub>. The fluorides were converted into sulfates, and the specimens were powdered [13]. The CM con-

**Fig. 2.** Photomicrograph of a graphitized rock specimen.

**Table 2.** Range of NM contents (g/t) in the Khankai graphitized rocks

Sample no.	Au	Ag	Pt	Pd	Rh	Ru	PGM	NM
04-2a	0.11–0.64	1.03–1.38	0.03–3.37	0.02–0.04	0.01	–	0.06–3.42	1.20–5.45
04-3	0.20	0.47	1.67	0.13	–	–	1.80	2.47
04-3a	0.77–0.98	0.28	0.03–2.14	0.02	–	–	0.05–2.16	1.05–3.42
04-5	0.20–49.0	0.10–1.62	0.02–0.05	0.19–1.09	4.05	–	0.21–5.19	0.51–55.8
04-7	0.23	1.10	1.44	0.17	–	–	1.6	2.94
04-7a	0.82–1.97	1.90–8.20	0.86	0.14–0.42	0.40–5.00	0.03	1.43–5.45	4.15–15.6
04-13	1.48	0.72–2.12	1.99	0.45	0.08–2.00	0.11–0.22	0.19–4.66	0.91–8.26
04-16	2.83–4.27	1.16–2.21	0.02–0.12	0.16–0.27	0.01	0.05–0.11	0.24–0.50	4.23–6.98
04-28	0.23	1.28	0.06	0.09	–	–	0.15	1.66
04-30	0.38	0.13	0.02	0.03	–	–	0.05	0.56
04-31	0.48–1.90	0.18–1.64	0.03	0.03–0.65	0.44–5.30	0.02–0.06	0.52–6.01	1.18–9.55
04-33	0.22–0.77	0.76–0.77	0.05–2.56	0.02–0.40	–	–	0.07–2.96	1.05–4.50
04-34	0.67–2.24	0.12–0.94	0.06–2.3	0.20–0.60	0.46–2.31	0.02–0.07	0.74–5.28	1.53–8.46
04-34a	0.55–2.50	0.27–1.12	0.11–0.29	0.05–0.41	1.25–1.65	0.05–0.20	1.46–2.55	2.28–6.17
04-35	0.77	0.64	0.01–2.57	0.02–0.19	–	–	0.03–2.76	1.44–4.17
04-40	1.36–6.96	1.18–1.36	0.04–0.06	0.06–0.57	0.01–0.40	0.02–0.10	0.13–1.13	1.67–9.45
04-76	0.04–0.21	0.17–1.90	0.01–0.03	0.06–0.27	0.01	–	0.07–0.31	0.28–2.42
04-80	0.37	0.26	0.02	0.35	–	–	0.37	–
04-101kr	0.57	0.77	1.68	–	–	–	1.68	3.02
04-107k	0.29	0.31	0.01	0.2	–	–	0.21	0.81
04-108	1.01	0.30–1.00	0.02–0.04	0.33	–	–	0.02–0.37	0.32–2.38
Average	0.68–1.40	0.66–1.48	0.44–0.95	0.07–0.30	0.32–0.99	0.014–0.037	0.51–2.28	2.18–7.61

Note: Anomalously high NM contents (>10 g/t) were omitted from calculation of the average content. Altered rocks: (04-2a) granite gneiss, (04-3, 04-13, 04-80) skarnoids, (04-3a, 04-5, 04-7a, 04-30, 04-31, 04-33, 04-34, 04-34a, 04-101kr) lamprophyre, (04-7, 04-108) vein quartz with graphite, (04-16, 04-40) black shale, (04-28, 04-76) plagiogneiss, (04-35) basic crystalline schist, (04-107k) marble.

tent in the samples was determined by the atomic emission spectroscopy with double jet plasmatron and the technique of multichannel registration of emission spectra (MAES). We could determine Ag, Au, Pd, and Pt (Rh and Ru in some samples). The detection threshold was 0.01–0.1 ppm. Application of scheme 2 is limited by the absence of a unified technique for the program record of interfering elements of the matrix (primarily, Fe, Cr, and Co).

**Scheme 3.** Samples (1–3 g) were fused together with niter, and the “candle end” obtained was decomposed in a mixture of HNO<sub>3</sub>, HCl, and HF (1: 1: 1). The CM content was determined by the EC TEA AAS method. We could determine Au, Pd, Pt, Rh, and Ir (detection threshold 0.1–3 ppb). In this analytical series, analysis 5 detected only traces of PGMs, suggesting either their migration together with the dust in the course of sample preparation or their removal as volatile compounds in the course of CM (graphite) burning [11, 12].

Analysis according to scheme 1 revealed that the PGM content in IR-2 formed during the IR-1 incineration accounts for 20–30% of the total PGM in the sam-

ple. Such an NM distribution among the first chloride solution, IR-1, and IR-2 suggests that no less than 90% CM in the samples studied are associated with graphite (CM). In our case, this fact is an additional obstacle for the determination of NMs, relative to rocks (ores) of typical black shales [11, 12].

Table 2 presents the results of analysis of NMs (Ag + Au + PGM). Based on schemes 1 and 2, contents of NMs range from 0.05 to 56 g/t. At the same time, the Pt content in 8 analyses (among 21 analyses) was higher than that of any other NM.

However, these data are preliminary ones, because the values of element determination show a very high scatter (150–200 times) in the series of two to five specimens. Hence, the samples (3–5 g) used in our analyses are insufficiently representative. This conclusion is supported by the determination of NM loss during the calcination of samples 25 and 30 g in weight (Table 2, specimen 04-34). In this case, the carefully averaged candle end was analyzed according to scheme 2. The absorbing solutions and gaseous phase products entrapped by the method [11] were analyzed by the EC TEA AAS method. The results show that the amount

of metal transferred to the gaseous phase is as follows (rel. %): Pd 50–70, Pt 30–50, Au up to 20, and (Ru + Rh) ~80. The reproducibility was  $\pm 25$ –30 rel. %. The average content was as follows (g/t): Ag  $1.92 \pm 0.44$ , Au  $0.65 \pm 0.18$ , Pt  $1.62 \pm 0.34$ , Pd  $0.42 \pm 0.14$ , Rh  $1.27 \pm 0.22$ , and Ru  $0.17 \pm 0.04$ . Thus, the NM concentration in the larger samples turned out to be close to the median value obtained for sample 04-34 (Table 2). Together with the reproducibility mentioned above, this fact suggests a better representativeness of the larger samples. Data in Table 2 represent the first approximate estimate of NM mineralization in the Ruzhino graphitized rocks. The contents of NMs (without consideration of anomalously high values) correspond to noble metal ores of the “middling poor” grade (g/t): Au 1.0, Ag 1.1, Pt 0.7, Pd 0.18, Rh 0.65, and Ru 0.02 (composite uncertainty  $\pm 40$ –60 rel. %).

Thus, the results obtained confirm the following facts. Our complex approach, which was used for the first time in black shales, can also be efficient for the analysis of NM contents in the new type of materials. Decomposition by fluorinate oxidation in the course of sample preparation minimizes the loss of NMs and enhances the reliability of their determination. Relative to the typical black shales, the rocks studied are characterized primarily by the association of NMs with graphite. Analysis of our data and that from the literature suggests that the PGMs and probably some part of Au occur as nanodimension metallorganic and/or organometallic clusters in the materials studied.

The NM analysis performed in our work is correct. The results obtained indicate that the studied and similar rocks can serve as a potential resource of the unconventional NM. The NM potential is enhanced by the occurrence of the graphitized rocks virtually near the day surface and their total distribution area.

The top priority task is to elucidate the NM occurrence mode in the CM, in general, and in the graphitized rocks, in particular. In addition, the systematic analysis of CM-containing objects requires the development of a standard composition standard. The standard will promote the elucidation of fundamental regularities in the genesis of such objects and methods of their utilization.

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