

Study of Reference Sample Candidate for the Noble Metal Contents (PGM, Au, Ag) in a Graphitized Rocks

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The difficulties of reliable determination of platinum group metals (PGMs) in gold-bearing carbonaceous ores have been noted in [1–5]. Even more problems arise when analyzing graphitized rocks of Primorye [6]. It is largely due to the fact that carbonaceous matter (CM) in these rocks consists of graphite, which prevented their complete decomposition. Another peculiarity is the practically complete absence of sulfides typical of black shales (BSs) [7]. There was a trial of certification of noble metal (NM) content in reference samples in some BS deposits: RSBS-1 (reference sample of black shale-1) and SLg-1 (Sukhoi Log-1) [3]. The PGM contents determined in those rocks by different techniques of sample preparation and analysis differed by 2–3 orders of magnitude [1–5]. At the same time, typically no problem with determination of Ag and Au in BS arose [1–4]. Furthermore, the strongly dropped PGM contents was registered when high temperature or oxygen-containing oxidants were applied during sample preparation [1–3]. Analysis of RSBS-1, SLg-1, and materials of the Natalka deposit based on the oxidative fluorination decomposition (OFD) method determined Pt, Pd, and Rh up to 10–20 g/t in total [5]. The presence of metal-organic or organometallic compounds in CM of rocks is the most probable channel for PGM losses. These volatile substances evaporate, being broken down in the typical preparation process for a reference sample [4]. Their possible presence was noted by almost all NM researchers in CM-bearing rocks of the world starting from the Zechstein of Europe [7]. The possibility of NM “conservation” and “storage” during thermal treatment of the CM of rocks up to 500°C was proved experimentally [8]. In

this connection, graphitized rocks of Primorye may become suitable candidates as reference samples certified on Ag, Au, and PGM contents and also as a new type of NM-bearing rock formations [9].

The aim of this work is optimization of operations in preparation of candidates for reference samples CRS–BS based on an average sample of graphitized rocks of Turgenevskoe graphite deposit. It was important to avoid significant losses of NM during preparation and analysis of samples and to receive analogous results in series of parallel determinations.

A sample of potentially metal-bearing rocks was taken in Ruzhinskii open-pit mine of the deposit. It was processed at room temperature by multistage cycles of crushing, sieving, and final grinding down to particles less than 100 μm in size. Milled rock (100 kg) was decreased down to 12 kg with the “ring and cone” method. The rock matrix consists of (wt %) SiO₂ 66.17, TiO₂ 0.29, Al₂O₃ 15.61, Fe₂O₃ 1.20, FeO 0.86, MnO 0.02, MgO 5.61, CaO 0.82, Na₂O 2.53, K₂O 3.01, P₂O₅ 0.10, S < 0.003, l.o.i. 3.25 (largely carbon), H₂O 0.17, Σ = 99.64 (analyst Zh.A. Shcheka, Far East Institute of Geology, Far East Division, Russian Academy of Sciences).

Several combinations of the chemical presampling with different NM analysis techniques were studied. The basic principle of sample preparation in the absence of a certified reference sample was the possibility of “internal” laboratory control of the similarity between flow charts of the results of independent analyses including all objects formed during the preparation stage, gas phase included. Due to the specificity of CM in CRS–BS and the very inhomogeneous NM distribution in rock samples, homogenization was optimized by mechanical activation (MA). After twofold MA on centrifugal elliptic activator TsEM (OOO Novits, Novosibirsk), the particle size did not exceed 40 μm (98% was less than 5 μm).

The NM content was determined in all products obtained after processing, including the cake after furnacing samples in oxygen (600–800°C). Gaseous fur-

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Table 1. Noble metals (g/t) in fractions of CRS–BS after OFD and F → Cl conversion

Sample	Ag	Au	Pd	Pt	Rh
Chloride solutions (OFD of the original sample)					
13-11	0.353	0.644	0.019	1.874	0.009
13-12	0.342	0.505	0.017	0.027	0.006
13-13	0.718	0.328	0.015	0.067	0.003
13-14	0.659	0.384	0.015	0.011	0.003
13-15	1.373	0.317	0.036	0.007	0.007
14-11	0.785	0.628	0.019	0.061	0.003
14-12	1.022	0.466	0.020	0.021	0.003
14-13	0.483	0.765	0.014	0.209	0.003
14-14	0.380	0.449	0.015	0.015	0.003
14-15	0.557	0.523	0.016	0.011	0.003
14-16	1.251	0.864	0.018	0.045	0.003
14-17	1.351	0.335	0.025	0.006	0.002
14-18	0.708	0.561	0.049	0.007	0.011
Chloride solutions (OFD of RI-1)					
14-11	–	0.025	0.11	0.018	0.019
14-12	–	0.023	0.14	0.004	0.027
14-13	–	0.023	0.15	0.022	0.023
14-14	–	0.008	0.14	0.021	0.015
14-15	–	0.006	0.13	0.009	0.013
14-16	–	0.065	0.14	0.009	0.016
14-17	–	0.054	0.17	0.010	0.020
14-18	–	0.021	0.11	0.007	0.019
IR-2, OFDS TJAP MAES method					
14-11	0.00090	Not detected	Not detected	0.0074	–
14-12	0.00011	"	0.0012	0.0052	–
14-13	0.00059	"	0.0004	0.0057	–
14-14	0.00042	0.0007	0.0003	0.0082	–
14-15	0.00045	Not detected	0.0009	0.0050	–
14-16	0.00019	Not detected	0.0003	0.0040	–
14-17	0.00044	0.0007	0.0005	0.0045	–
14-18	0.00146	Not detected	Not detected	0.0033	–

Note: Samples not subjected to MA are shown in bold.

nancing products (outgases) were trapped by 2M HCl + 1M N₂H₄ · HCl solution and analyzed by method [4]. Oxidative fluorination decomposition (OFD) was carried out in melted potassium tetrafluorobromate KBrF₄ (PTFB) [6]. Obtained fluorides were converted into water–chloride solutions and separated from the insoluble residue (IR). Detailed descriptions of OFD pro-

cesses including those for BS, especially with details of analytic techniques, are given in [4–6, 10–12]. Powdered fluorides obtained through the OFD procedure in many cases were additionally presampled with application of sulphatization (OFDS process [10, 12]) and further analyzed by atomic emission spectral analysis, as described above. NM determination in a powder of sul-

Table 2. Noble metals in different fractions of CRS–BS (g/t)

Conditions and objects	Ag	Au	Pt	Pd
Without mechanoactivation				
Direct OFDS TJAP MAES of cake (20–30 g, $n = 3$)*	0.65 ± 0.29	0.38 ± 0.01	0.77 ± 0.06	0.12 ± 0.03
Solutions absorbing roasting gases (20–30 g)	Not detected	0.008 ± 0.0007	~ 0.001	~ 0.002
Direct OFDS TJAP MAES of batches (~ 5 g, $n = 13$)	0.32 ± 0.48	0.21 ± 0.32	0.11 ± 0.11	0.16 ± 0.14
Multistep analysis (~ 5 g, $n = 13$)	1.44 ± 1.28	0.56 ± 0.20	0.21 ± 0.10	0.19 ± 0.52
With mechanoactivation				
Direct OFDS TJAP MAES of cake (20–30 g, $n = 3$)*	0.67 ± 0.2	0.35 ± 0.04	0.68 ± 0.12	0.12 ± 0.02
Solutions absorbing roasting gases (20–30 g)	Not detected	0.015 ± 0.010	0.007 ± 0.006	0.010 ± 0.009
Direct OFDS TJAP MAES of batches (~ 5 g, $n = 13$)	3.82 ± 3.68	0.31 ± 0.09	0.97 ± 0.17	0.29 ± 0.04
Multistep analysis (~ 5 g, $n = 13$)	n.a.	0.45 ± 0.10	1.45 ± 0.32	0.180 ± 0.04
Losses during roasting	n.a.	0–0.10 $\sim 20\%$	0.3–0.830 70%	0.1–0.1730 60%

* Batch (g) and number of analyses (n).

fated fluoride cake was performed by atomic-emission spectral analysis using a double-jet arc plasmatron and registration technique MAES (method TJAP MAES) [10]. The experimental installation for TJAP MAES is described in [10, 12]. In the prepared samples, Ag, Au, Pd, and Pt were detected (detection threshold 0.01–0.1 ppm) [10, 12]. If interfering elements (Fe, Cr, etc.) occur in great amounts, powdered samples of the final insoluble residue were analyzed by the TJAP MAES method to control completeness of NM recovery. Calibration of the NM concentration scale was performed using geostandards having a different mineral matrix: platinum ore SARM-7 (South Africa) and NMs on the graphite collector SOG-13 (Russia).

After conversion of fluorides into chlorides, NMs from solution were preconcentrated into an organic extragent (mixture of di-2-ethylhexyldithiophosphoric acid with alkyl-aniline). Then NMs were detected by atomic-absorption spectrophotometry (AAS) with electrothermal atomization (EC TEA AAS method [13, 14]). A PerkinElmer spectrophotometer was applied (model 503 with an electrothermal atomizer HGA-74 and deuterium background correction, system 3030 with atomizer HGA-600 and background correction based on the Zeeman Effect). Conditions of analytical signal optimization are described in [14]. Assessed NM are Au, Pd, Pt, and Rh; detection limit 0.1–3 ppb. The results are given in Tables 1 and 2.

The phase composition of CRS–BS was studied on an X-ray diffractometer for general applications of the DRON-type, equipped by the Seifert-RM gauging system in monochromatized radiation $\text{CuK}\alpha$ in step-by-step surveying with a space 0.05° in the angle range

$8^\circ < 2\theta < 65^\circ$ (a set of $n \times 10^3$ – 10^4 impulses in the most intensive reflex with control parameters of stability and reproducibility of diffractograms). Decryption of diffractograms was performed on the JCPDS database (Fig. 1). CRS–BS consists of quartz ($\alpha\text{-SiO}_2$) with plagioclases (dominating are albite $\text{Na}(\text{Si}_3\text{Al})\text{O}_8$ and variously arranged anorthite $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$). Comparison with the results of silicate analysis suggests that the source rock involved not less than 60% quartz. After treatment of CRS–BS in KBrF_4 and leaching of the fluoride cake in HCl_{conc} , the insoluble residue (IR-1) consisted of K_2SiF_6 , K_2NaAl_6 , KAlF_4 , and $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ with 3–5% SiO_2 and a phase of isostructural KMnF_3 or KFeF_3 (Fig. 1).

IR spectra of a source sample were obtained on a SCIMITAR Fourier IR spectrophotometer in the range 400–4000 cm^{-1} . Sample batches (1.0 mg) tableted in thoroughly dried KBr were working samples. The Fourier IR spectrum of CRS–BS includes absorbance bands from tetrahedral and octahedral groups with Al–O and Si–O bonds at 420–660, 781, and 1100 cm^{-1} , absorbed moisture in the area of 1640 cm^{-1} , and strongly bound water at 3450 cm^{-1} (Fig. 2). Within the broad intense absorbance band 1000–1400 cm^{-1} at 1040 cm^{-1} , there is a clearly expressed component possibly referring to valence variation bonds $sp^2\text{-C-OH}$. Weak absorbance peaks 1430 and 1560–1570 cm^{-1} relate to oscillations of functional groups $sp^2\text{-COOH}$ and $sp^2\text{-C=O}$. In combination with $sp^3\text{-C-OH}$ bonds, this circumstance suggests that carbonaceous matter of CRS–BS is notably oxidized (i.e., oxygen is present in it).

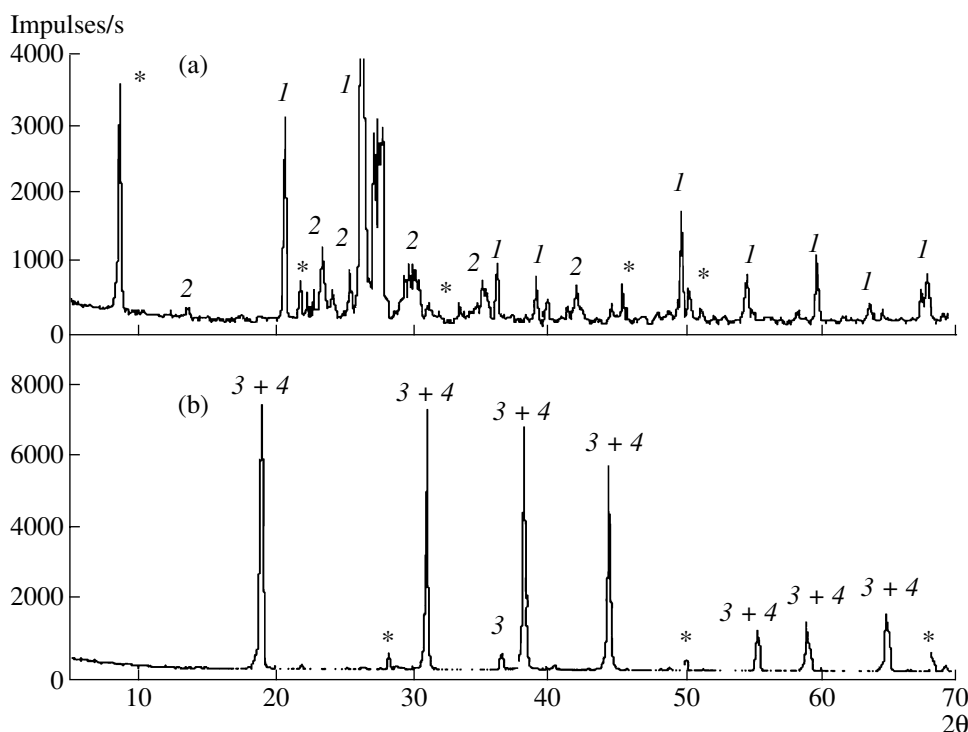


Fig. 1. X-ray diffractograms of CRS-BS sample: (a) original sample (1—quartz, 2—albite); (b) insoluble residue (IR-1) after conversion F-Cl (3— K_2SiF_6 , 4— K_2NaAlF_6). Asterisks denote phases of uncertain composition.

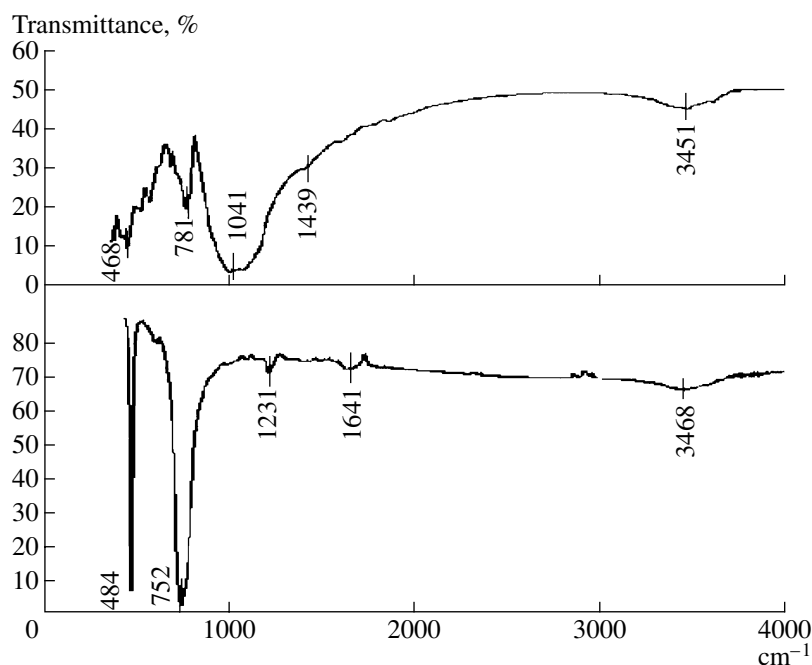


Fig. 2. Fourier IR-spectra of CRS-BS sample and product of its F-Cl conversion: (top) original sample (quartz, albite); (bottom) residue insoluble (RI-1) after F-Cl conversion (K_2SiF_6 , K_2NaAlF_6).

The Fourier IR spectrum of RI-1 fixes the absorbance bands at 484 and 752 cm^{-1} corresponding (data by [14]) to valence and deformational vibrations of Si-F bonds in K_2SiF_6 (Fig. 2). Weak bands at 575–608 cm^{-1} may refer to valence vibrations of Al-F bonds in simple

and complex aluminum fluorides [14]. Weak absorbance bands at 1230 and 1330 cm^{-1} related to valence oscillations of sp^3 -C-F bonds in CF and CF_2 groups (data from [15]) attest to the presence of materials similar to fluorinated graphite CF_x ($x > 0.8$) in IR-1. The

wide absorbance band in the high-frequency spectrum area with a center at 3468 cm^{-1} refers to H-bonds of water (or even H_3O^+) with domination of acid groups. Weak bands of absorbed moisture are also noted near 1641 cm^{-1} and very weak absorbance bands $\text{sp}^2\text{-C=O}$ at 1430 and $1560\text{--}1570\text{ cm}^{-1}$.

Judging from IR-spectra and X-ray phase analysis, the largely fluoride composition of IR-1 shows that, after treatment of the fluorinated cake in HCl_{conc} , potassium hexafluorosilicate and aluminum fluoride, its composition did not experience any significant conversion. Those substances form by the reaction of KBrF_4 with oxides of silicon, aluminum, and calcium of the mineral matrix [10, 11]. Such uncommon phenomena may take place if fluoride particle agglomerates of the matrix rock are covered with a thin, rather compact hydrophobic external layer. They hinder direct contact of particles with the HCl aqueous solution. In our case only fluorocarbon material may compose the hydrophobic pellicle resistant to concentrated HCl . Its composition is close to highly fluorinated CF_x ($x \approx 0.8\text{--}1.0$) and forms during the interaction of the original oxidized carbonaceous material with potassium tetrafluorobromate. The presence of CF_x is supported not only by the IR spectrum, but also by the appearance of a loose dingy-yellow IR-1 precipitate on a filter when separating the chloride solution. Neither water nor the HCl solution moisten the precipitate. An analogous situation was noted when analyzing all other samples of the Turgenevskoe deposit by OFD [6]. This circumstance once more demonstrates the radical distinction of CM in graphitized rocks of Primorye from those in ores of Natalka and Sukhoi Log.

Table 1 shows that one-act decomposing of CRS–BS with KBrF_4 is not enough. More than 90% of PGM oxidized in the course of OFD is blocked in IR-1 and does not penetrate into the chloride solutions. This specific feature differentiates rocks of Turgenevskoe deposit [6] from BSs of the Natalka and Sukhoi Log deposits [4, 5]. The specific features of CRS–BS carbonaceous matter decomposing in KBrF_4 revealed required repeating the OFD procedure with IR-1 and separation of IR-2 to control the similarity of results by the OFDS method [10, 12]. Only two procedures of successive breaking up with PTFB (both samples and IR) ensured sufficient NM recovery.

Significant discrepancies in the Au and Ag determinations in 13 samples (Table 2) not subjected to MA suggest that in the CRS–BS sample gold micrograins occur. It explains the spread of Au content values (g/t): from 0.25 to 2.82 with an average of 0.38–0.56. A similar situation exists for silver. Mechanoactivation of CRS–BS samples decreases but does not exclude the spread of analysis results.

The behavior of NMs during sample preparation and multistage analysis reveals important features of their occurrence in rocks. This means that PGM are

connected mostly to rather oxidized CMs, largely graphite. This conjecture is supported by analyses of solutions absorbing the gas phase when furnacing; they include from 30 to 90% of the total PGM sum. The completeness of PGM recovery from furnacing out-gases by the above-mentioned method still requires additional control. Unlike PMGs, gold and silver most probably occur in native form and intermetallic compounds Au_xAg_y . Distribution of the latter causes the spread of the determination results.

The described presampling schemes of CM-bearing samples in combination with different instrumental techniques of NM determination for the first time provided acceptable similarity of analytical results of such persistent objects. Homogenization by mechanoactivation significantly increased the validity of analysis results. In combination with direct determination of NMs by the OFDS TJAP MAES method, it allows creation of relatively quick testing of similar objects, black shale included. The described candidate CRS–BS as one of the persistent objects with high NM content is suitable as a geostandard of CM-containing products and opens the possibility of its certification for noble metal concentration.

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