ISSN 1028-334X, Doklady Earth Sciences, 2009, Vol. 425, No. 2, pp. 213–215. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.I. Khanchuk, N.V. Berdnikov, A.A. Cherepanov, N.S. Konovalova, D.V. Avdeev, 2009, published in Doklady Akademii Nauk, 2009, Vol. 424, No. 5, pp. 672–675.

GEOLOGY

First Finds of Platinoids in Black-Shale Sequences of the Bureya Massif (Khabarovsk Region and Jewish Autonomous Okrug)

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Received September 16, 2008

DOI: 10.1134/S1028334X0902007X

The problem of the platinum-metal potential in black-shale sequences has recently attracted the attention of geologists [1–5], since highly carbonaceous rocks of different origins are considered to represent the most probable future nontraditional natural source of gold and platinoids. Black shales with high carbon contents are widespread in the Bureya Massif. Single chemical analyses revealed in them elevated concentrations of platinoids ranging from 0.0*n* to *n* g/t [6]. The forms of platinoids occurring in these rocks remain, however, unknown, which hampers the assessment of their recoverable reserves and development of technologies for their extraction. In this connection, the purpose of this work is the study of the composition, morphology, and grain-size of platinoids in these rocks.

Using the method of the scanning electron microscopy with an energy-dispersion analyzer (SEM-EDA), we found and first studied platinoids in black shales of the Sutyr and Kimkan sequences in the eastern Bureya Massif. These sequences represent constituents of the Upper Riphean–Lower Cambrian Khingan Group. They are subjected to greenschist metamorphism, structurally uniform, and characterized by elevated carbon contents.

The Sutyr Sequence (PR_1st) constitutes an extended (75 × 5 km) tectonic block in the Khingan deep-seated fault zone. It is largely composed of carbonaceous shales, phillites, and metasiltstones with C_{org} concentrations of 1 to 22%. Shales are sulfidized to different extents and enclose locally thin quartz stringers. Sulfides (pyrite and subordinate pyrrhotite, chalcopyrite, arsenopyrite, covelite, and marcasite) form fine-grained (up to 1 mm) impregnation, rare stringers, and lenses up to 0.5–2.0 cm long. Carbonaceous material consists of fine dispersed amorphous matter and fine graphite scales sized 0.01–0.03 mm. The semiquantitative analyses revealed gold, platinum, and palladium (up to 0.1, 0.04, and 0.01 g/t, respectively) in rocks of the sequence.

Based on the lithological features, the Kimkan Sequence ($Є_1$ km) is subdivided into the lower siliceous–terrigenous and upper terrigenous subsequences. The lower subsequence ($Є_1$ km_1) 900–1070 m thick is represented by clayey and siliceous–clayey frequently carbonaceous shales, phthanites, siltstones, sandstones, limestones, dolomites, jasper-like siliceous rocks, hematite and magnetite–hematite ores, and rhyolites. The upper subsequence ($Є_1$ km_2) 800–900 m thick is composed of sandstones, siltstones, shales with interbeds of phthanites, limestones, rhyolitic tuffs, and basalts. The content of carbonaceous matter locally grading into graphites due to contact metamorphism amounts to 3–9 and, less commonly, 12–25%. Carbonaceous rock varieties frequently contain sulfide (pyrite, pyrrhotite) mineralization.

In the Sutyr Sequence, platinoids are studied in samples of fine-grained carbon-bearing sulfidized quartz–sericite shales taken from the left bank of the Sutyr River (Fig. 1, Point *1*); such a lithology is characteristic of the entire sequence. For the Kimkan Sequence, black shales, magnetite–hematite carbon-bearing shales, ores of the Kimkan deposit as well as products of their alteration (yellow ocher), and dolomites were analyzed (Fig. 1, Point *2*). Shales and ores are established to contain platinum and Os iridium, while only the latter is found in dolomites.

Platinoids in these rocks are characterized by the following main occurrence forms: finely dispersed

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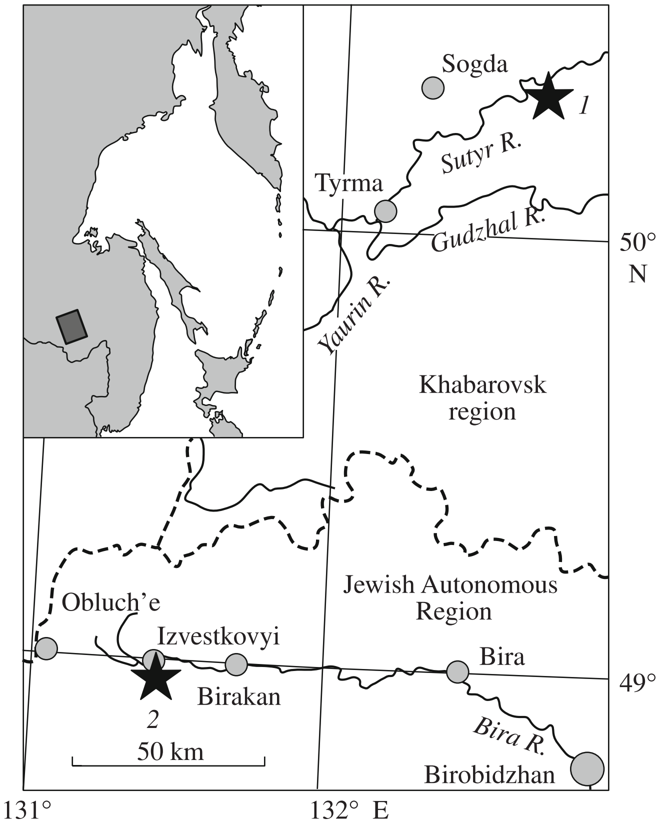

Fig. 1. Sampling sites for the study of platinoids (asters) in rocks of the Sutyr (*1*) and Kimkan (*2*) sequences.

(Fig. 2a), plates and fine wires (Fig. 2b), crystalline (Figs. 2c, 2e), and subcrystalline aggregates (Fig. 2d). The first three varieties are unique to platinum, crystals characteristic of platinum and Os iridium, and subcrystals characterize platinum and palladium compounds. Finely dispersed (<100 nm) platinum forms aggregates, which include also Ag (up to 6.6), Cu (27.6–36.8), Ni (4.0–4.9), Ti (up to 3.3), Si (9.5–10.3), O (18.2–24.0), and C (2.1–4.0), in addition to Pt (16.6–28.5).[1] Plates frequently have 3–5 specimens together consisting of Pt (57.1–84.2), Cu (up to 1.0), O (4.6–6.2), and C (10.9–36.6). Fine wires are most rich in platinum (91.6–92.9). They also consistently contain Au (3.9–5.2) and C (3.2). Plates form frequently hollow (case-shaped) and true cubic crystals. The former are occasional and contain Pt (58.8–82.3), Fe (up to 1.3), Ti (up to 6.9), Ca (up to 2.0), Si (up to 2.0), O (5.5–17.2), and C (7.5–25.0). True platinum crystals usually form schistose aggregates and consist of Pt (66.6–75.7), Fe (up to 2.0), O (8.7–17.3), and C (13.7–15.8). The occurrence of oxygen and carbon in microcrystalline platinum aggregates indicates transportation of Pt in the form of carboxyl and carbonyl complexes [7]. The relatively high oxygen content reflects the oxidized state of ore-bearing fluid, which favored crystallization of native platinum.

Contents of platinoids in black shales

	Rh, mg/t	Pd, mg/t	Pt, mg/t	Au, mg/t
	With ignition			
Solution	–	11.4	–	170.6
Sediment	1.5	11.1	9.3	167.3
Total concentration	1.5	22.5	9.3	337.9
	Without ignition			
Solution	4.0	13.8	–	44.9
Sediment	0.2	16.5	7	280.0
Total concentration	4.2	30.3	7	324.9

Note: Data are averaged for two parallel samples.

Palladium registered as a complex subcrystalline or amorphous compound consisting of Pt (8.2), Sn (35.6), Pd (1.3), Cu (1.2), Fe (1.1), Ti (1.3), Si (2.7), and O (48.6). Aggregates of Os iridium are frequently confined to marginal parts of microhollows that were formed after sulfide leaching, where they occur in intergrowth with quartz and rutile. The energy-dispersion analysis reveals in these aggregates Ir (34.3–43.5), Os (15.4–23.1), O (23.0–35.6), C (2.7–7.4), and an admixture of REE represented by Yb (up to 2.1), Dy (up to 3.2), Gd (up to 2.4), and subordinate Rb (up to 2.2), Co (up to 1.3), Ti (up to 1.4), and Si (up to 2.1).

Prior to platinoid analysis, black shales were subjected to chemical dissolution through their multiple successive treatment by aqua regis, HF, and HCl both after ignition (3 hour at 700°C) and without the latter. The obtained solution was analyzed by the ICP-MS method with preliminary concentration by precipitation together with tellurium. The residue after dissolution was again studied by the SEM-EDA method and after alloying with Na_2O_2 and leaching was analyzed for precious metals (Table 1). Analysis didn't reveal platinum in acidic solutions, but half of palladium goes into solution irrespective of roasting procedure. SEM-EDA studies revealed that reside consists largely of rutile, zircon, Os iridium, and platinum grains. Abundant aggregates of Os iridium appeared to be most resistant to acid dissolution (Fig. 2e, inset). Its abundant grains are registered even after fusion with Na_2O_2 and leaching.

Thus, black-shale sequences of the Bureya Massif contain visible platinoids in different occurrence forms. In our opinion, finely dispersed agglomerates containing many other elements represent the earliest platinum form. Subsequent recrystallization and, probably, redeposition result in partial cleaning of platinum from admixtures and formation of platy and crystalline forms. Iridium and osmium are concentrated in Os iridium, which is characterized by high oxygen and carbon contents.

Platinum, iridium, and osmium are practically undeterminable in examined rocks by chemical analysis, when acid dissolution of samples is used. Such proper-

[1] Hereinafter, in wt %.

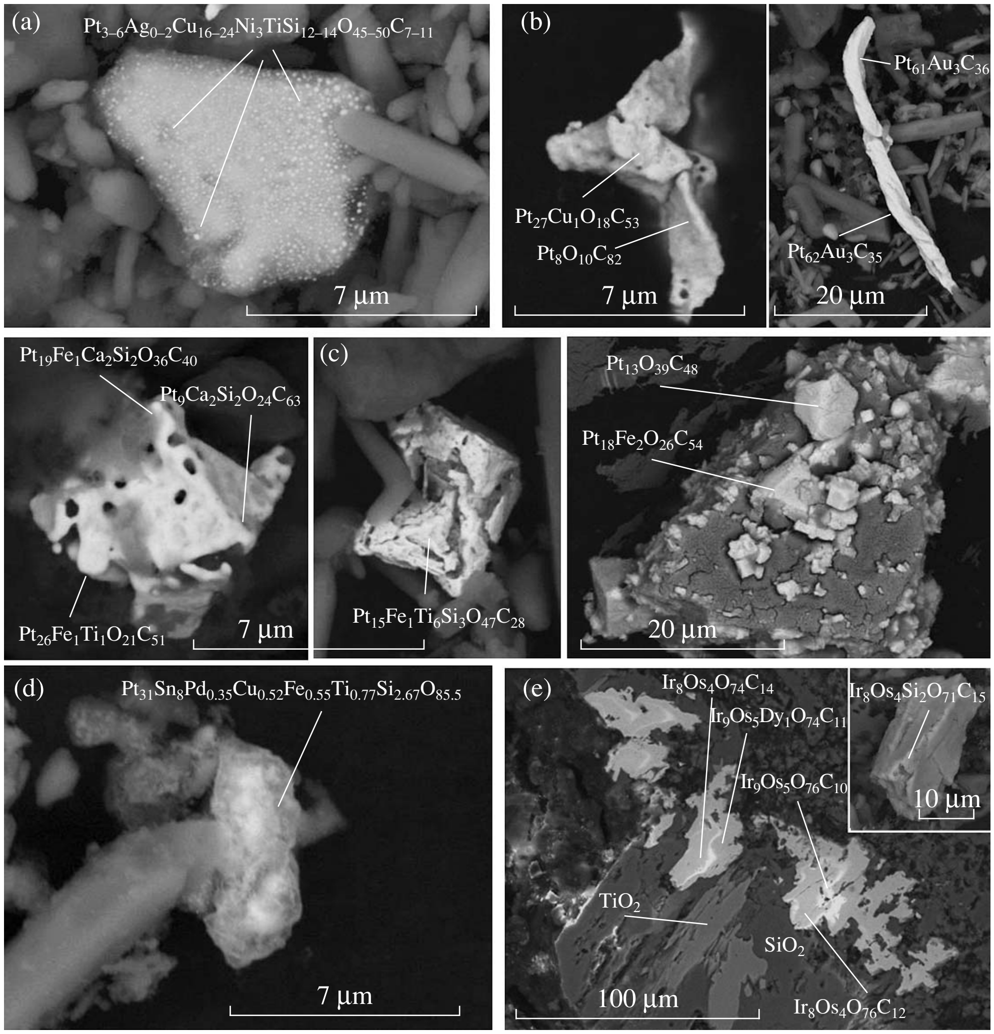

Fig. 2. Inclusions of platinoids in black shales of the Bureya Massif: (a–d) Kimkan Sequence, after acid dissolution: (a) aggregate of finely dispersed material, (b) plates and fine wires, (c) case-shaped crystals and aggregates of crystals, (d) subcrystalline (amorphous?) aggregate; Os iridium in the rock matrix from the Sutyr Sequence (polished section).

ties of black shales are likely explained by the occurrence of carbon in them, which "screens" aggregates of noble metals protecting them from acid dissolution. In addition, the SEM-EDA analysis demonstrates that carbon and/or its oxidized forms always occur in platinoid aggregates increasing their stability substantially. In this situation, at the beginning of acid dissolution, platinoids from the surface layer of aggregates are washed out, while insoluble carbonaceous compounds form a protecting crust on their surface, which inhibits further dissolution.

Our studies show that black shales of the Sutyr and Kimkan sequences contain platinoids mostly in the native form. Inclusions of noble metals are from a few to tens of microns in size. At the same time, their abundance in rocks is significant, which provides, along with the native character of the useful component, certain prospects for their practical use.

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