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Some observations on the determination of platinum group elements and gold in black shales

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The concentration levels and distribution features of the platinum group elements (PGE) in black shales with high carbon content from the Bureya Massif, Far East Russia are discussed. This study compares PGE and gold (Au) values in black shale ores from the eastern Bureya Massif. Mineralogical studies using SEM–EDS on PGE-bearing inclusions in black shales reveal that they always contain O and C along with Pt, Pd, Ir and Os. It is believed that PGE are present in the form of organometallic compounds which are extremely resistant to any exposure, including acid dissolution and fire assay procedures. There is a lot of variation in the concentration values obtained using different analytical methods. Observations, problems and possible causes for the erratic and low recoveries of Au and PGE in the highly carbonaceous black shales are discussed.

Keywords: Black shales, gold, organometallic compounds, platinum group elements, volcanic complexes.

The average concentration of platinum group elements (PGE) and gold (Au) in rocks is extremely low, less than 3 ng/g (ref. 1). Because of the low concentration levels and inhomogeneous distribution of the elements in different rocks, large amounts of sample (usually > 20 g) are commonly taken for the pre-concentration steps such as fire assay before instrumental determination. It is well known that most of the PGE deposits are hosted by mafic–ultramafic plutons in association with chromite and sulphides. However, several studies in recent times have shown that PGE also exist in the sedimentary marine environment such as black shales2,3. Black shale-hosted PGE deposits have recently become promising sources of PGE and many other metals, and several unconventional PGE accumulations and new data on PGE distribution have been reported from marine black shales of China, Canada, USA, Czech Republic, Finland, Poland and Russia. In this context, the problems of the platinum metal potential in black shale sequences have attracted the attention of geologists4–8 because highly carbonaceous rocks of different origins are considered to represent the most probable nontraditional natural source of Au and PGE in the future. Black shales with high carbon content are widespread in the world in general and in the Bureya Massif, Far East Russia in particular. In general, Au and PGE are collected by nickel sulphide fire assay (NiS–FA) into a NiS button as a separation and pre-concentration step before the determination of these elements by inductively coupled plasma mass spectrometry (ICP–MS)9,10.

Some chemical analyses showed the presence of elevated concentrations of PGE ranging from 0.1 to 40 g/t in the black shales11. However, reproducibility of these analyses was low, and the forms of platinooids occurring in these rocks remained unknown. There is need to understand the factors which are hampering their recovery and development of technologies for their extraction.

Using scanning electron microscope with energy dispersive spectrometry (SEM–EDS), PGE-bearing inclusions in black shales of the Sutyr and Kimkan sequences in the eastern Bureya Massif have been studied (Figure 1). These sequences represent constituents of the Upper Riphean–Lower Cambrian Khingan Group. They are sub-
jected to greenschist metamorphism and structurally are uniform and characterized by elevated carbon content.

The Sutyr sequence constitutes an extended (75 × 5 km) tectonic block in the Khingan deep-seated fault zone. It is largely composed of carbonaceous shales, phyllites and metasiltstones with organic carbon (Corg) concentrations of 1–22%. Shales are sulfidized to different extents and are enclosed locally within quartz stringers. Sulphides (pyrite and subordinate pyrrhotite, chalcopyrite, arsenopyrite, covellite and marcasite) form fine-grained (up to 1 mm) impregnation, rare stringers and lenses up to 0.5–2.0 cm.

On the basis of lithological features, the Kimkan sequence is subdivided into the lower siliceous–terrigenous and upper terrigenous subsequences. The 900–1070 m thick lower subsequence is represented by clayey and siliceous–clayey frequently carbonaceous shales, phthianites, siltstones, sandstones, limestones, dolomites, jasper-like siliceous rocks, hematite and magnetite–hematite ores and ryolitites. The 800–900 m thick upper subsequence is composed of sandstones, siltstones, shales with interbeds of phthianites, limestones, ryolitic tuffs and basalts. The carbonaceous matter locally grades into graphites due to contact metamorphism amounting to 3–9% and less commonly to 12–25%. Carbonaceous rock varieties frequently contain sulphide (pyrite and pyrrhotite) mineralization.

In the Sutyr sequence, platinoids are studied in samples of fine-grained, carbon-bearing, sulphidized quartzsercite shales taken from the left bank of the Sutyr River (1, Figure 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 analysed (2, Figure 1). Shales and ores have been established to contain Pt and Os–Ir, whereas only the latter is found in dolomites.

PGE in these rocks are characterized by the following main occurrences forms: finely dispersed (Figure 2a), plates and fine wires (Figure 2b), crystalline (Figure 2c and 2e) and subcrystalline aggregates (Figure 2d). The first three varieties are unique to Pt, crystals characteristic of Pt and Os–Ir, and subcrystals characteristic of Pt and Pd compounds.

Finely dispersed (<100 nm) Pt forms aggregates, which include also Ag (up to 6.6 wt.%), Cu (27.6–36.8 wt.%), Ni (4.0–4.9 wt.%), Ti (up to 3.3 wt.%), Si (9.5–10.3 wt.%), O (18.2–24.0 wt.) and C (2.1–4.0 wt.%), in addition to Pt (16.6–28.5 wt.%), (ref. 1). Plates frequently have 5–6 specimens together consisting of Pt (57.1–84.2 wt.%), Cu (up to 1.0 wt.%), and C (10.9–36.6 wt.%), Fine wires are most rich in Pt. They also consistently contain Au (3.9–5.2 wt.%), and C (3.2 wt.%). Pt frequently forms hollow (case-shaped) and true cubic crystals. The former are occasional and contain Pt (58.8–82.3 wt.%), Fe (up to 1.3 wt.%), Ni (up to 6.9 wt.%), Ca (up to 2 wt.%), O (5.5–17.2 wt.%), and C (7.5–25.0 wt.%). True Pt crystals usually form schistose aggregates and consist of Pt (66.6–75.7 wt.%), Fe (up to 2.0 wt.%), O (8.7–17.3 wt.%), and C (13.7–15.8 wt.%). The occurrence of oxygen and carbon in microcrystalline platinum aggregates indicates transportation of Pt in the form of carboxyl and carbonyl complexes12.

Pd registered as a complex sub-crystalline or amorphous compound consists of Pt (8.2 wt.%), Sn (35.6 wt.%), Pd (1.3 wt.%), Cu (1.2 wt.%), Fe (1.1 wt.%), Ti (1.3 wt.%), Si (2.7 wt.%), and O (48.6 wt.%). Aggregates of Os–Ir are frequently confined to marginal parts of microhollows that were formed after sulphide leaching, where they occur in intergrowth with quartz and rutile. EDS analysis reveals the following in these aggregates: Ir (34.3–43.5 wt.%), Os (15.4–23.1 wt.%), O (23.0–35.6 wt.%), C (2.7–7.4 wt.%), and an admixture of rare earth elements represented by Yb (up to 2.1 wt.%), Dy (up to 3.2 wt.%), Gd (up to 2.4 wt.%), and subordinate Rb (up to 2.2 wt.%), Co (up to 1.3 wt.%), Ti (up to 1.4 wt.%), and Si (up to 2.1 wt.%). The compositional characteristics of these inclusions represent the organometallic nature of compounds which are extremely resistant to decomposition techniques, including acid dissolution and fire assay.

Results of PGE data using different analytical techniques are presented in Table 1. It can be seen that analytical methods, which use chemical or fire assay decomposition of samples, show low concentration of

![Figure 1](image-url)  
**Figure 1.** Sampling sites for the study of platinoids (asterisk) in rocks of the Sutyr (1) and Kimkan (2) sequences.
precious metals. This may be due to the high stability of PGE–Au–C–O compounds to chemical influence, including fire assay. Khanchuk et al.\(^4\) have discussed various techniques of sampling and analysis which vary significantly, the losses of these metals because of the difficulties in breaking the metal–carbon chemical bonds. On the other hand, Mitkin et al.\(^13\) reported direct evidence of PGE volatilization from black shale materials when processed in the presence of oxygen. They have also found that in Au-bearing black shale ores, PGE are present as organo-

\(^{9}\text{XRF, X-ray fluorescence spectrometry; }^{10}\text{AAS, Atomic absorption spectrometry; }^{11}\text{ICP–MS, Inductively coupled plasma mass spectrometry; }^{12}\text{GD–MS, Glow discharge mass spectrometry; }^{13}\text{NAA, Neutron activation analysis.}\)
Seismic vulnerability and risk in the Himalayan township of Mussoorie, Uttarakhand, India

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Rapid visual screening technique has been resorted to for assessing seismic vulnerability and risk in the Himalayan township of Mussoorie that falls in Zone IV of the Earthquake Zoning Map of India. Damage during an earthquake in this zone is expected to reach MSK intensity VIII. A total of 3344 structures in 11 residential wards of the town were surveyed in the field. Data collected in the field were analysed under GIS environment which suggests that a total of 615 (18%) buildings show high probability of Grade 5 damage and very high probability of Grade 4 damage class. The economic loss likely to be incurred is estimated to be of the order Rs 238.85 crore in the township of Mussoorie alone. Modest estimates suggest that 369 persons might sustain grievous injuries in this event. The study highlights the fact that some of the lifeline buildings are under severe threat and are required to be retrofitted or replaced on priority basis.

Keywords: Damage grade, rapid visual screening, risk, seismicity, vulnerability.

SUBDUCTION of the Indian plate beneath the Eurasian plate has resulted in the consumption of the intervening oceanic plate and eventual collision of the alien land masses. This event caused deformation, upliftment, metamorphism and shearing of the sediments deposited in the hitherto intervening ocean basin together with the rock mass in the vicinity of the collision front. This resulted in the evolution of the Himalayan mountain chain. Since the collision around 55 Ma, India has been undergoing at a rate of 45–50 mm/yr (refs 1 and 2). GPS measurements indicate that India is moving northeast at a convergence rate of 55 mm/yr, of which 18–22 mm/yr is accommodated within the Himalayas and the remaining convergence is taken up further north in Tibet and Asia. The ongoing northward convergence of India produces active deformation in the Himalayas, Tibet and adjoining areas and is responsible for seismic activity in the entire region.

The Himalayan mountain arc together with the adjoining Shillong plateau and western Assam has witnessed four great earthquakes ($M_w \geq 8.0$) in the previous 110 years, i.e. 1897 western Assam earthquake, 1905 Kangra earthquake...

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