

Os-rich nuggets from Au-PGE placers of the Maimecha-Kotui Province, Russia: a multi-disciplinary study

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Summary

Geological, mineralogical and Os isotopic data for detrital PGE-mineralization derived from the Guli and Bor-Uryah ultramafic massifs, within the Maimecha-Kotui Province (the northern part of the Siberian Platform, Russia), are presented for the first time. The detrital platinum-group minerals (PGM) are dominated by Os–Ir–(Ru) species, which is typical for ophiolites or Alpine-type complexes. However, the PGM assemblage in the placers investigated is similar to that derived from zoned platiniferous clinopyroxenite–dunite massifs (also known as Uralian-, Alaskan-type and Aldan-type massifs). The unique features of the Au-PGE placers at Guli are (1) the dominance of Os-rich alloys over other PGM and Au, and (2) the considerable predicted resources of noble metals, particularly osmium.

Dominant chromite, olivine and clinopyroxene inclusions recorded in Os–Ir–(Ru) alloys imply that they were derived from ultramafic sources (e.g., chromitite, dunite and clinopyroxenite). The first in situ osmium-isotope measurements by laser ablation - multiple collector - inductively coupled plasma mass spectrometry of different, intimately intergrown, PGM (e.g., laurite and Os-rich alloys) in various nuggets from Guli have revealed low $^{187}\text{Os}/^{188}\text{Os}$ and γOs values. They yield a very narrow range of $^{187}\text{Os}/^{188}\text{Os}$ (0.12432 to 0.12472) and γOs (–2.39 to –2.07). These values are indicative of a common chondritic or subchondritic mantle source of PGE. $^{187}\text{Os}/^{188}\text{Os}$ and γOs values of Os-rich alloys, derived from the Bor-Uryah massif, are different (i.e.,

γ Os ranges from -2.67 to -1.30). The mineral-isotopic data obtained are consistent with the conclusion that the PGM were derived from parent ultramafic source rocks. Os-isotope model ages in the range of 495 to 240 Ma constrain the age of ultramafic protoliths in the northern part of the Siberian Craton. The variation in $^{187}\text{Os}/^{188}\text{Os}$ values for detrital PGM, where the provenance source is unknown, is considered to be a useful technique for distinguishing parent bedrock sources.

Introduction

The unique properties of osmium, the rarest platinum group element (PGE), led to its application in many areas of human activity. However, world production of osmium remains low (i.e. 500 kg per annum), mainly because of a limited number of geological sources. The most important osmium supplier to the world market in the 20th century are the complex PGE-bearing uranium–gold paleoconglomerates at the Witwatersrand, South Africa: about 15 tonnes of osmium and iridium have been mined up to date (*Cousins*, 1973; *Benevol'sky* and *Zubatareva*, 1993 and others). The average PGE composition for this deposit (in wt.%) is: Os – 38, Ir – 35, Ru – 14, Pt – 12, Rh – 1.

In Russia, osmium is produced in insignificant amounts (several dozens of kilograms per annum) as a by-product of copper–nickel ores of the Noril'sk–Talnakh type and from platinum placers associated with the clinopyroxenite–dunite massifs of the Urals, Far East and Aldan (also known as Uralian- and Aldan-type massifs). In contrast, Alpine-type ultramafic massifs of the Urals (Voikaro-Syn'in, Nurali, Kempirsai, etc.), Koryakia (Tamvatnei, Krasnogorskii, Chirynei, etc.), which are specialized for refractory PGE (e.g., Os, Ir and Ru) (*Volchenko* and *Koroteev*, 1990; *Melcher* et al., 1994; *Palandzhian* et al., 1994; among others), are not accompanied by commercial placers. Reserves of known placers linked to this dunite–harzburgite association do not exceed several hundred kilograms.

Placers of refractory PGE and gold associated with the Guli clinopyroxenite–dunite massif (Figs. 1, 2) situated within the Maimecha-Kotui Province in the Northern part of the Siberian Craton show uncommon features [e.g., mineral associations and the considerable predicted resources of noble metals, and, in particular, osmium (*Malitch* et al., 1995, 1996, 1998; *Auge* and *Malitch*, 1997; *Malitch* and *Lopatin*, 1997a, b; *Badanina* and *Malitch*, 1998; *Malitch* and *Badanina*, 1998, etc.)]. These features are the subject of this paper. In particular, we direct our emphasis to mineral chemistry of Os-rich minerals derived from the Guli and Bor-Uryah ultramafic massifs, for which Os-isotopic composition has been obtained by laser-ablation attached to multiple collector inductively coupled plasma mass spectrometry (LA MC-ICP-MS) and negative thermal ionization mass spectrometry (NTI-MS). Finally, we present first results of in-situ osmium-isotope analyses for intimately intergrown laurite and Os-rich alloy in order to focus on the origin of PGE-mineralization, the source of the PGE, and to place age constraints on the formation of the ultramafic protoliths.

Geological setting and sample location

The nuggets studied were derived from placer deposits closely associated with the Guli and Bor-Uryah ultramafic massifs. Since the beginning of the sixties, increas-

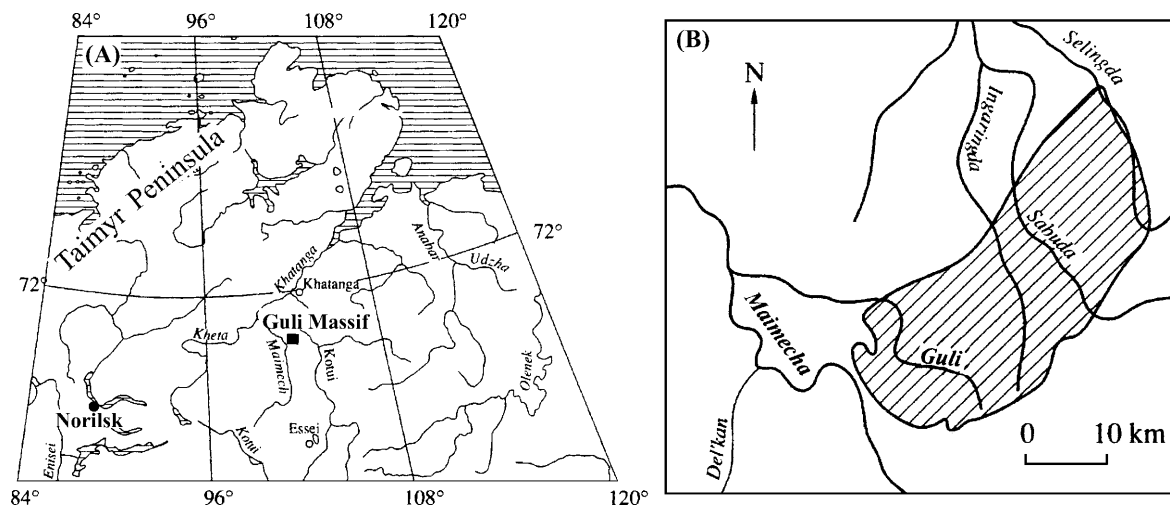


Fig. 1. Location of **A** the Guli clinopyroxenite–dunite massif; **B** the drainage system in the area of the Guli massif. Shaded area refers to the exposed part of the Guli ultramafic massif

ing scientific interest has been devoted to these massifs (e.g., *Butakova and Egorov, 1962; Zhabin, 1965; Vasiliev and Zolotukhin, 1975, 1995; Egorov, 1991; Kogarko et al., 1995; Malitch, 1999* and references cited therein).

The main geological characteristics of these ultramafic massifs and associated placer deposits are presented below. Particular emphasis is given to the placers, because (1) these are less known in the literature and (2) all of our investigated samples were taken from them.

Geological features of ultramafites of the Guli and Bor-Uryah massifs

The Guli massif, located in the northern part of the Siberian Craton occupies an area of about 2000 km² and is thus the world's largest clinopyroxenite–dunite massif. Aspects of the geology have been summarized by *Malitch and Lopatin (1997a, b)* and *Malitch (1999)*. The Guli massif is controlled by the Taimyr-Baikal and Enisei-Kotui paleo-rift structures. The exposed part (600 km²) of the massif is mainly composed of an ultramafic complex (Fig. 2), represented by dunite, chromitite, wehrlite and magnetite-bearing clinopyroxenite. Dunite (Fo₈₅₋₉₁) predominates, forming a crescent-shaped, plate-like body 30 km long and 10–15 km wide covering an area of approximately 450 km², which dips moderately (i.e., 15–20°) to the northwest. A restricted number of bedrock-hosted PGM in dunite and chromitite have been identified by *Balmasova et al. (1992)*, *Malitch and Rudashevsky (1992)* and *Malitch (1999)*.

To the southwest, the ultramafic complex is overlain by the Maimechian ultramafic volcanic rocks (known as maimechites), whereas in its central part, it is penetrated by stock-like bodies of the 220–240 Ma Maimecha-Kotui ijolite–carbonatite complex (Fig. 2), which occupies an area of less than 35 km² (*Egorov, 1991; Kogarko et al., 1995* and references cited therein). On the basis of recent Os-isotope data, the Guli ultramafic complex is dated as Late Devonian – Early Carboniferous with model ages of around 370 Ma (*Malitch, 1999*).

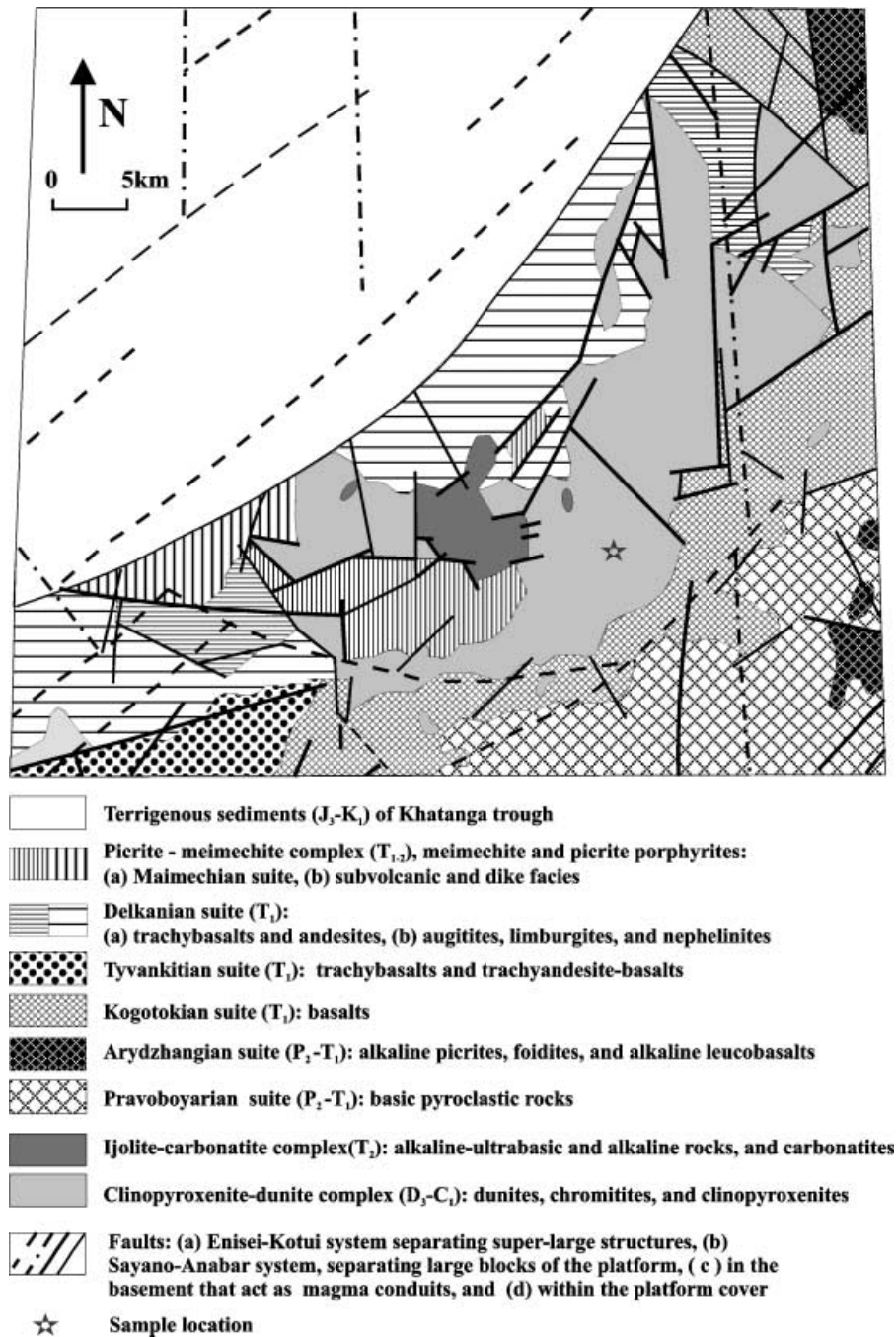


Fig. 2. Schematic geologic map of the Guli massif area (modified after *Malitch and Lopatin*, 1997b). Sample site is indicated

The Bor-Uryah massif of ultramafic rocks with an area of 18.5 km² is located 100 km to the south of the Guli massif. The massif intrudes Late Proterozoic (Riphean) and Cambrian terrigenous-carbonaceous rocks, forming a dome-like structure (*Egorov*, 1991; *Kogarko et al.*, 1995; *Malitch*, 1999). Core-zone olivinite

(metadunite?) comprising olivine and titanomagnetite grades into dunite with nodular chromitite in the outer part of the massif. The core-zone olivinites were also intruded by vein-like coarse-grained ore-rich olivinite (up to 20–50% of titanomagnetite and perovskite), alkaline syenite and rarely by melteigite and calcite carbonatite. Based on K–Ar dating the age of phlogopite from veins ranges from 215 to 225 Ma (Egorov, 1991).

Geological features of placer deposits

The placer deposits of the Guli massif are associated with recent and Upper Quaternary alluvial sediments of the rivers Ingaringda, Sabyda, Guli, Selingda and their tributaries (Malitch et al., 1998). Both fluvial sediments and terrace beds contain PGM and gold. The precious metal nuggets are particularly concentrated in terrace beds and occur preferentially in a clay-rich interbed with boulders, especially close to the boundary of unconsolidated sediments and bedrock. A schematic longitudinal section of recent and Upper Quaternary sediments along the Ingaringda river valley is shown in Fig. 3.

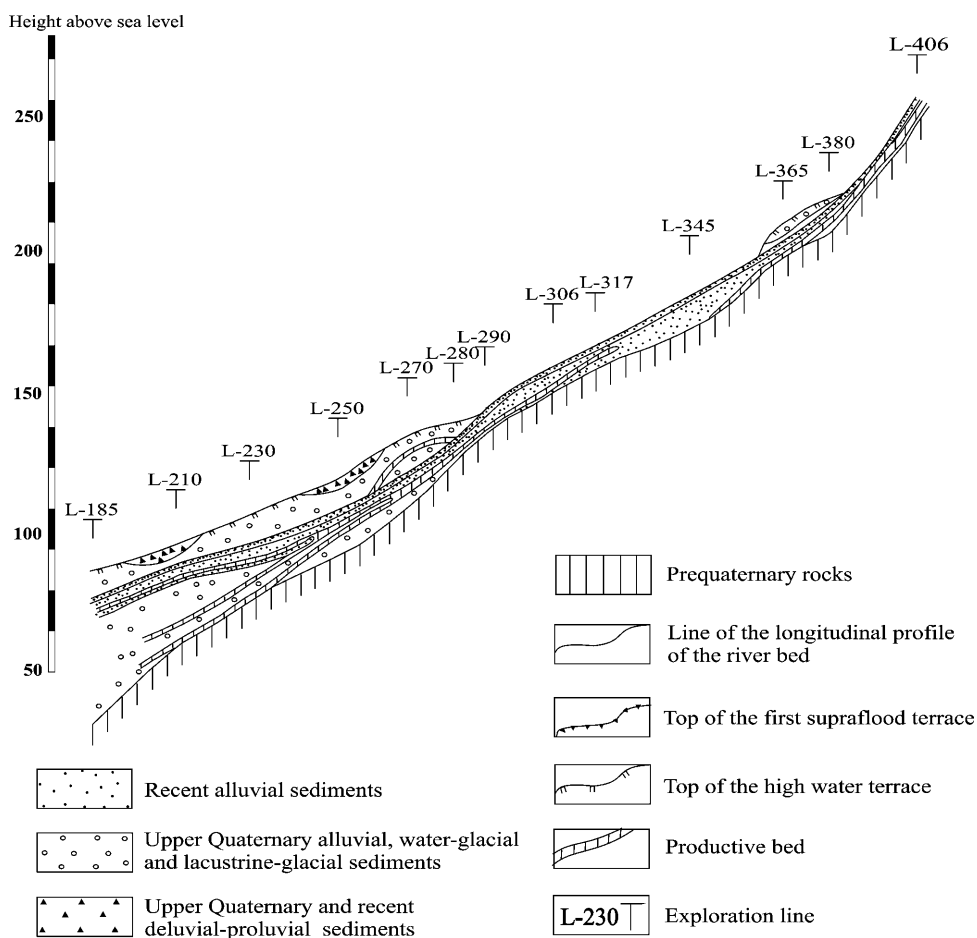


Fig. 3. Longitudinal section of the Ingaringda River (modified after Malitch et al., 1998)

The granulometric composition of alluvial PGM is determined by five size classes (in millimetres): $<0,25 - 0,50$ (56%); $0,125 - 0,25$ (33%); $0,5 - 1,0$ (9%); $+1$ (about 1%) and $<0,125$ (around 1%). The granulometric composition of heavy gold concentrates is defined by the following five size ranges (in descending order, mm): -2 (26%); >4 (22%); $2 - 4$ (20%); $0,5 - 1,0$ (20%); $0,25 - 0,50$ (11%); $0,125 - 0,25$ (1%).

Short transport distances are indicated by the preservation of crystal shape of the detrital PGM (Fig. 4). The Au-PGE placers that developed within the recent drainage network in the area of the Guli massif have an alluvial origin and, probably, a minor fluvioglacial component. The placers were formed during

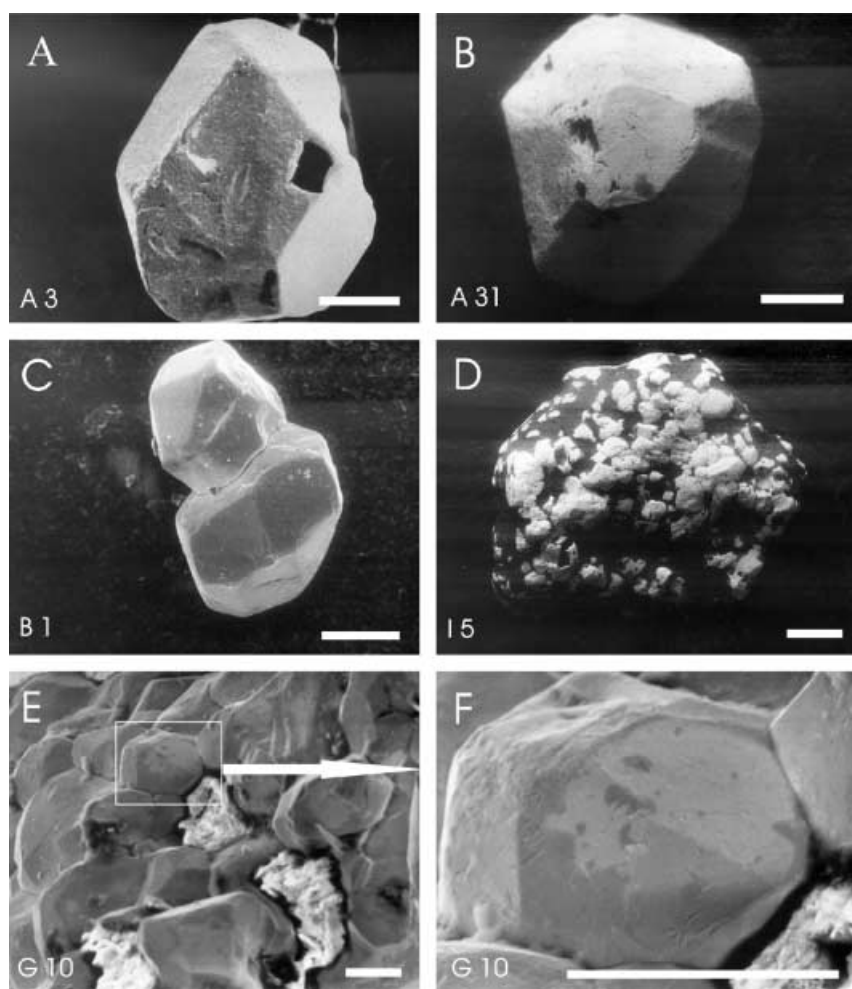


Fig. 4. Morphology of Os-rich nuggets from the Quaternary sediments of the Ingarinda River; euhedral single crystals of osmium (A nugget A 3, and B nugget A 31), crystalline aggregates of osmium (C nugget B 1, and E nugget G 10) and iridian osmium (D nugget I 5); F detail of Fig. 4E, showing well preserved crystal of osmium in a polyphase aggregate (nugget G 10). Scanning electron microscope images were obtained by secondary (A, C, E and F) and back-scattered (B and D) electrons. Scale bar is 100 μm

the unroofing and disintegration of ultramafic rocks, the subsequent release of precious-metal mineral phases, which are proximal to their source.

Au-rich minerals at Guli consist of native gold, Pd-rich gold, electrum AuAg, Au-rich silver and Au–Cu alloy. Among the gold-rich nuggets Au–Ag alloys with varying content of Ag (15 to 60 at.% Ag) rimmed by native gold are most abundant. Nuggets of Au–Cu alloy associated with various Au–Ag alloys and rarely observed Pd-rich (up to 11 at. % Pd) gold with a number of Pd- and Pt-rich mineral inclusions (telluropalladinite Pd_9Te_4 , mertieite-II $\text{Pd}_8(\text{Sb,As})_3(?)$, and sperrylite PtAs_2) have been also identified and will be presented elsewhere.

The majority of detrital PGM associated with the Guli massif have Os–(Ir–Ru)-dominated compositions. Their morphology, physical and chemical properties, textural features, and Os-isotopic composition were summarized by *Malitch* et al. (1995) and *Malitch* (1996, 1999). A variety of PGM, oxide and silicate inclusions characteristic of such Os–(Ir–Ru) alloys, and unusual polycomponent alloys of the Ru–Os–Ir–Pt–Fe system were first reported by *Malitch* and *Auge* (1998) and *Malitch* and *Badanina* (1998). Compositional and structural data for Pt–Fe alloys have been presented in detail by *Malitch* and *Thalhammer* (2002).

Os-rich nuggets including Os-rich alloys and Ru–Os sulphides (nuggets G 1-12, G 2-2, G 23-5 among other PGM nuggets), were sampled during prospecting in the area of the Ingarinda River (Line 365) in the southern part of the Guli massif (Fig. 3).

The central part of the Bor-Uryah massif represents an erosion crater, which is rimmed by a circular mountain ridge composed of Cambrian and Riphean terrigenous rocks. The main physiographic structure in the area is the Buor-Uryah river valley, which originates at the confluence of two streams in the central part of the massif and flows northeastwards through the circular mountain ridge (*Malitch*, 1999). PGM nuggets investigated in this study (nuggets BU-4, BU-7, BU-8, BU-9, BU-13) were obtained in the course of PGE exploration from Quaternary and recent sediments in the north-eastern part of the massif.

Proposed noble metal resources

Resources of the Ingarinda and Guli rivers with a sufficient number of exploration lines were evaluated by category P_1 (Table 1). For the other areas the forecast resources were calculated according to P_2 and P_3 categories (Table 1). P_1 refers to closer spacing of sampling lines than P_2 and P_3 . Delineation of the productive bed, during evaluation of the resources of category P_1 , was based on a cut-off grade of 0.1 g/m^3 . In evaluating the resources according to P_1 category, the method of linear blocks (cross-sections) was used. The respective exploration lines were assumed as block boundaries within the placer area. Three layers were distinguished: “fluvial”, “upper” and “lower”. Individual block setting and resource calculations were done for each block. The resources for each metal, areas and volumes in each layer and the whole placer were determined by summing up the respective data for each block.

Exploration and evaluation conducted by the Polar Exploring Party since 1990 suggest that the valleys of the Ingarinda and Guli rivers are the most promising areas within the Guli massif. In particular, the placer located along the upper to middle waters of the Ingarinda River (Figs. 1b, 3) measures $26.40 \times 0.18 \text{ km}$, at a

Table 1. *Estimated resources of PGE and gold in the area of the Guli massif*

Metal, Rivers	Estimated resources by categories, kg			Total, kg
	P ₁	P ₂	P ₃	
PGE				
Ingaringda River	2124	–	1987	4111
Selingda River	–	54	9500	9554
Sabyda River	–	55	–	55
Vostochnaya River	–	36	–	36
Total	2124	145	11487	13756
Gold				
Guli River	1848	–	1207	3055
Sabyda River	–	293	2882	3175
Maimecha River	–	106	108	214
Total	1848	399	4197	6444

Data after *Malitch et al.* (1998)

thickness of 1.2 m, with the average PGE grade 0.383 g/m³ and reserves of several metric tons.

The discovery of other genetic types of placers – coastal-marine, buried and in weathering crusts – should not be ruled out. Noble metal mineralization in the bedrock is expected here (*Malitch et al.*, 1995) along with the recently discovered gold-PGE placers. The total resources of noble metals (PGE and gold) in the area of the Guli massif are estimated as dozens of metric tons.

According to prospectivity forecasts by Polar Exploring Party, the Quaternary sediments in the Bor-Uryah area are promising for PGE-mineralization, with grades up to 0.265 PGE g/m³. However, for a more accurate estimation, more prospecting work in the area is required.

Analytical methods

Initially, the morphology and chemical composition of PGM nuggets were investigated by using a Camscan electron microscope-microanalyzer equipped with a Link-10 000 energy dispersive system at Mekhanobr-Analyt JSC, St.-Petersburg, Russia. In a second stage, after preparation of polished grainmounts, the noble metal minerals and their inclusions were analysed quantitatively with a Cameca SX50 electron microprobe (BRGM, Orleans, France): acceleration voltage 25 kV, beam current 20 nA, counting time 6 seconds. The standards used were: Cr₂O₃ for Cr, AsGa for As, pyrite for Fe and S, stibnite for Sb, and pure metals for all other elements. The X-ray lines used were K_α for Ni, Cu, Fe, S, Co and Cr, L_α for Sb, Te, Au, Rh, Ir, Pt and Ru, and L_β for Os, Pd and As. A PAP correction program was used. Several interferences that could not be avoided were corrected by calculation. Silicates were analysed using a standard program (acceleration voltage 15 kV, beam current 12 nA, counting time 6 seconds). Additional microprobe analyses were also carried out on an ARL-SEMQ microprobe with four

wavelength-dispersive spectrometers (WDS) and equipped with a LINK energy dispersive analyser (EDS) at the Institute of Geological Sciences (Mineralogy and Petrology Group), University of Leoben, Austria. Details of this analytical procedure are described by *Malitch et al.* (2001b). A total of about 1500 quantitative analyses have been performed on 290 PGM nuggets from Upper Quaternary and recent deposits of the Ingarinda and Guli rivers.

After microprobe analysis, the PGM grains from the Guli and Bor-Uryah massifs were investigated by laser ablation (LA) and multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at the Institute of Archaeometry, TU Bergakademie Freiberg. LA was performed with a Microprobe II laser ablation device (VG, Nd: YAG laser, 266 nm, pulse duration 3 ns, energy output to sample up to 4 mJ, ablation spot size up to 50 μm). The aerosols generated by LA were transferred by a He stream to the MC-ICP-MS (ThermoElemental Axiom, multi-collector version with 9 Faraday cup detectors, resolution 400). The signals were measured at m/z 183 (W), 184 (W + Os), 185 (Re), 186 (W + Os), 187 (Re + Os), 188 (Os), 189 (Os), 191 (Ir) and 193 (Ir). Technical details of the method and principal factors that influence the accuracy of LA MC-ICP-MS analyses are presented elsewhere (*Becker and Dietze, 2000; Junk, 2001* and references cited therein).

Finally, selected PGM nuggets were removed from the polished section and the osmium isotopic composition was determined on individual grains by negative thermal ionization mass spectrometry (NTI-MS) using a modified MI-1320 instrument (*Kostoyanov, 1998; Kostoyanov et al., 2000*) at the Department of Isotope Geology, All-Russia Geological Research Institute (VSEGEI), St.-Petersburg, Russia. Precision of the osmium isotope determinations, based on the reproducibility of isotope ratios in one series of parallel runs, was found to be 0.3%. With this method, it is possible to analyse individual PGM grains with a mass of 10^{-7} g and osmium content >10 wt.%. Further details of the method and analytical precisions are given in *Malitch et al.* (2000). The data obtained were normalized to the $^{190}\text{Os}/^{188}\text{Os}$ ratio of 1.98379 ± 0.00002 according to the "osmium-DTM-standard" measured by NTI-MS on the mass-spectrometer MAT-262 (*Tuttas, 1992*).

Chemical composition of minerals

To avoid confusion with osmium and iridium as elements, we refer to the Os-rich alloy grains as osmium (Os content >80 at.%), iridian osmium (Os, Ir) and osmian iridium (Ir, Os). Members of the Ru–Os sulphide solid solution series show a complete compositional spectrum, from laurite RuS_2 to erlichmanite OsS_2 . Mineral chemistry of Os-rich alloys and Ru–Os sulphides is illustrated by Figs. 5–8, whereas chemical composition of PGM and of the most abundant inclusions hosted by Os-rich alloys are presented in Tables 2–4. Further details on the PGM, oxide and silicate phases documented in the nuggets will be presented elsewhere.

Os, Os–Ir and Ir–Os alloys

The majority of nuggets at Guli, both single crystals (e.g., subhedral, euhedral) and aggregates of euhedral crystals (Fig. 4), are Os-rich alloys (osmium, according to the classification by *Harris and Cabri, 1991*) with considerable variation of Ir and

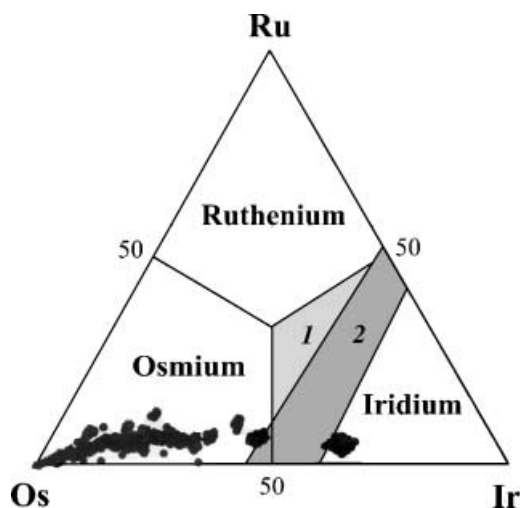


Fig. 5. Composition of Os-rich alloys at Guli in coordinates Ru–Os–Ir, at.%. 1 – rutheniridosmine; 2 – miscibility field

Ru from one nugget to another. The sum of Os + Ir + Ru in an alloy is, as a rule, 99 wt.% (Table 2). Minor elements, systematically detected in some grains, include Pt [up to 2.54 wt.%, with an average of 2.21 wt.% (standard deviation 0.14)], Cu [up to 0.56 wt.%, with an average of 0.42 wt.% (standard deviation 0.05)]. Other elements, such as Pd (up to 1.04 wt.%), As (up to 0.42 wt.%) and Rh (up to 0.63 wt.%) have been sporadically detected within different grains but are not systematically present even in a single grain. The compositions of osmium minerals plotted on the Os–Ir–Ru ternary diagram (Fig. 5) reveal two trends: (1) Ru is inversely proportional to Os in the interval from 100 to 80 at.%; and (2) Ru does not vary with the replacement of osmium by iridium in an interval of less than 80 at.%.

Osmian iridium (Ir, Os), intergrown with iridian osmium (Os, Ir), has also been observed (Table 2, an. 9; Fig. 5). In contrast to Os-rich alloys from Guli, those from Bor-Uryah are dominated by iridian osmium (Table 2, an. 10–12, 14; Figs. 6a, 7A). No intergrowths with other minerals nor any inclusions in iridian osmium were observed at Bor-Uryah, whereas at Guli Os-rich alloys are frequently intergrown with Ru–Os sulphides, chromite, olivine and clinopyroxene (Figs. 6 b–d, f, 8 a, b, e). Further, a wide spectrum of PGM inclusions, as well as oxide, sulphide and silicate inclusions, has been documented in the osmium minerals (Tables 3 and 4). We distinguish five types of inclusions: (1) monophase inclusions of silicates (forsteritic olivine, serpentine) and oxides (chromite, chrome-bearing magnetite); (2) polyphase silicate and oxide inclusions; (3) monophase base metal sulphide (BMS) inclusions (pentlandite, chalcocite and djerfisherite); (4) polyphase inclusions of BMS and PGM (Pt–Fe alloy, moncheite PtTe_2 and telluropalladinite Pd_9Te_4); and (5) monophase and polyphase PGM inclusions [i.e., laurite $(\text{Ru, Os})\text{S}_2$, erlichmanite $(\text{Os, Ru})\text{S}_2$ – $(\text{Os, Ir})\text{S}_2$, irarsite IrAsS and rutheniridosmine (Os, Ir, Ru)].

Laurite–erlichmanite series

Minerals of the laurite–erlichmanite series RuS_2 – OsS_2 are usually documented in association with osmium and iridian osmium, either as interstitial phases between

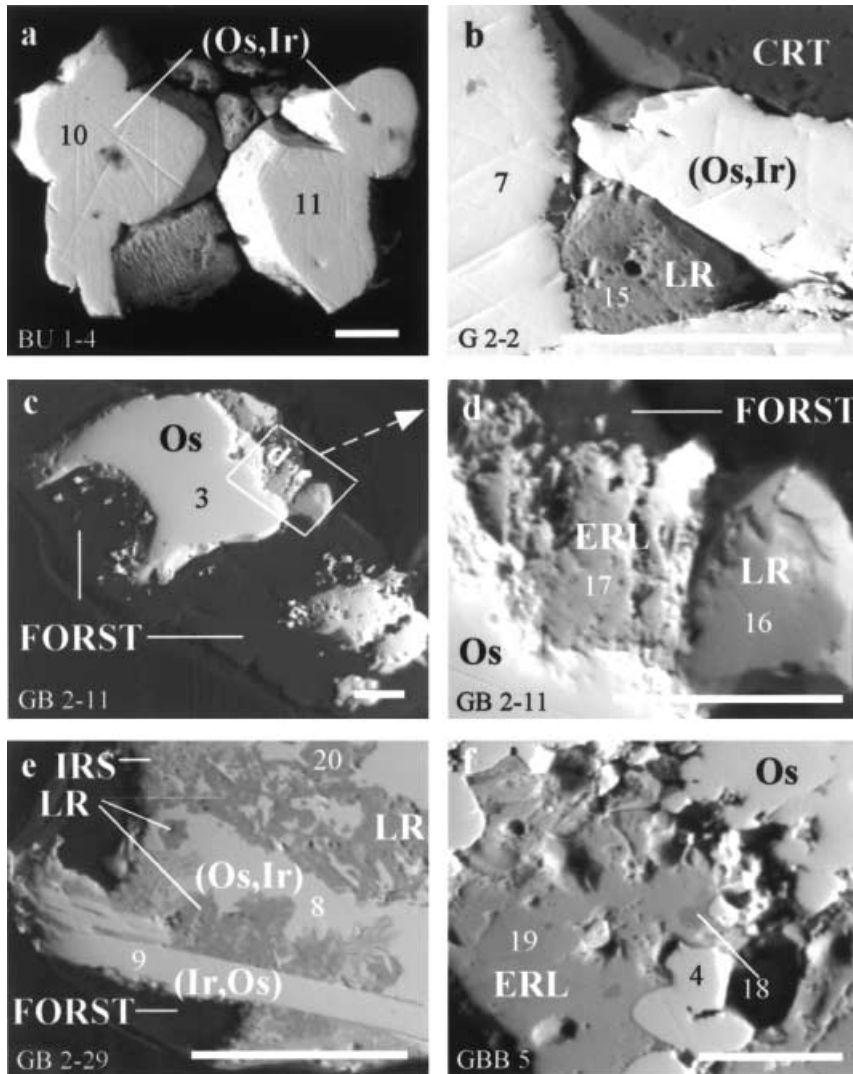


Fig. 6. Back-scattered electron images of polyphase nuggets from the Bor-Uryah (a) and Guli (b–f) massifs. *Os* osmium, (*Os, Ir*) iridian osmium, (*Ir, Os*) osmian iridium, *LR* laurite, *ERL* erlichmanite, *IRS* irarsite, *CRT* chromite, *FORST* forsterite; numbers 3, 4, 7–11, 15–20 denote areas of electron microprobe analyses corresponding to the same numbers in Tables 2 and 3. Scale bar is 50 μm

the Os-rich alloy grain boundaries (Fig. 6b), or as a “negative” inclusion in the alloy. However, in rare examples, complex intergrowths may be present (Fig. 6c–f). Other PGM identified, in such polymineral nuggets, are iridian osmium (Os, Ir), osmian iridium (Ir, Os), Pt–Fe alloy, irarsite (IrAsS) and forsterite Mg_2SiO_4 .

Ru–Os sulphides at Guli display large variations in Ru number [$100 \cdot \text{Ru} / (\text{Ru} + \text{Os})$], ranging from 99 to 2 (Fig. 7B, C and Table 3). This trend is similar to that of Ru–Os sulphide inclusions from chromitites at Kempirsai, Urals (Melcher et al., 1997; Garuti et al., 1999) and Kraubath, Eastern Alps (Malitch et al.,

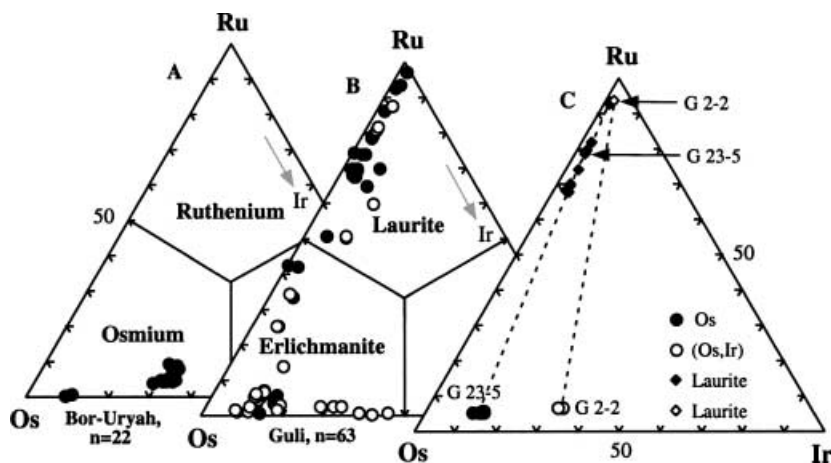


Fig. 7. Composition of Os-rich alloys from Bor-Uryah (A), Ru–Os sulphides at Guli (B) and intimately intergrown PGM from nuggets G 23-5 and G 2-2 (C) in the ternary diagram Ru–Os–Ir, at.%. Open circles refer to inclusions, full circles to intergrowths with alloys

in press). Examples of such phenomena are exemplified by several nuggets (Figs. 6c, d, f, 7B, C, 8a–c; Table 3, an. 16–19, 21–23): nugget G 23-5 shows the intimate zoning of at least 3 various laurite compositions (Ru numbers 94, 81 and 71), whereas nuggets GB 2-11 and GBB 5 reveal association of 2 distinct Ru–Os sulphides (laurite and erlichmanite) with osmium (\pm forsterite). The composition of laurite, when plotted on the Os–Ir–Ru ternary diagram (Fig. 7B), shows common Ru substitution for Os. In contrast, erlichmanite compositions are dominated by uncommon Os substitution for Ir, with low Ru concentrations (Os from 67.61 to 37.95 wt.%, Ir from 31.94 to 5.50 wt.%, and Ru from 9.78 to 0.35 wt.%). Thus, two solid solution series are present in erlichmanite: (1) usual Os for Ru substitution in continuous solid solution between erlichmanite OsS_2 and laurite RuS_2 (Ru number 2 to 43); and (2) uncommon Os for Ir substitution between erlichmanite OsS_2 and unnamed IrS_2 (Fig. 7B; Table 3). The latter substitution trend for erlichmanite inclusions is similar to that observed in the Os–Ir alloy (Fig. 5), implying that the composition of inclusions is inherited from the alloy. Minor elements detected in erlichmanite include Pt, Fe, Pd, Ni and As (up to 0.74, 1.42, 0.48, 2.35 and 0.35 wt.%, respectively).

Osmium-isotopic composition of minerals

The $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ values of detrital PGM of the Guli and Bor-Uryah massifs are presented in Tables 5 and 6. Since the concentration of Re in all samples appears to be less than 0.05 wt.%, the isotopic effect caused by *in situ* radioactive decay of ^{187}Re is negligible. Consequently, the value of $^{187}\text{Os}/^{188}\text{Os}$ in the PGM corresponds to that in the source of the ore material at the time of PGM formation. The $^{187}\text{Os}/^{188}\text{Os}$ ratios in Os-rich alloys and Ru–Os sulphides from Guli vary between 0.12432 and 0.12472 (Table 5, an. 1–12, Table 6, an. 1; Fig. 8). Therefore, isotopic fractionation among these Os-rich minerals is insignificant. However, the Os-rich alloys from Bor-Uryah show variations: $^{187}\text{Os}/^{188}\text{Os}$ ratio in PGM

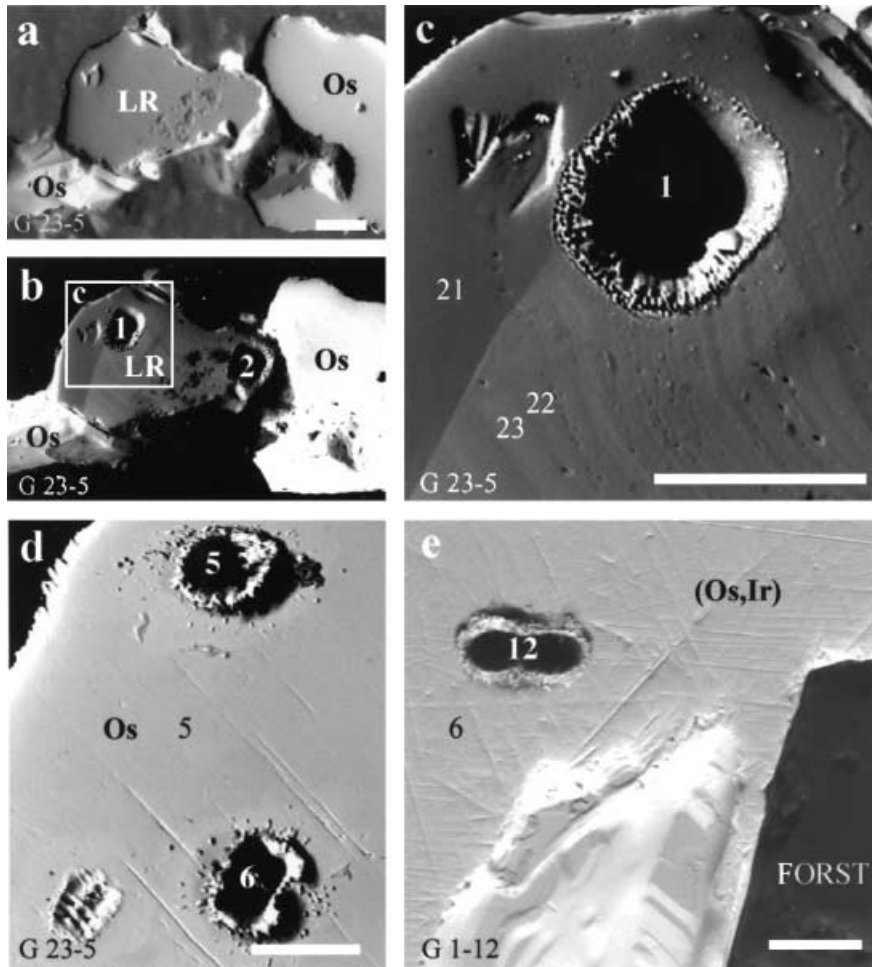


Fig. 8. Back-scattered electron images of Os-rich nuggets (G 23-5 and G 1-12) from the Guli massif before (a) and after (b–e) laser ablation MC-ICP-MS. (*Os*, *Ir*) iridian osmium, *Os* osmium, *LR* laurite, *FORST* forsterite; details of nugget G 23-5 show laurites of different composition (c) and osmium (d). Numbers 5, 6, 21–23 denote areas of electron microprobe analyses corresponding to the same numbers in Tables 2 and 3. Numbers in black holes (1, 2, 5, 6 and 12) indicate sectors of laser ablation MC-ICP-MS analyses, which correspond to numbers in Table 5. Scale bar is 50 μm

recorded by both isotopic techniques vary from 0.12396 to 0.12571 (Table 5, an. 13–18; Table 6, an. 11 and 12). The dispersion of $^{187}\text{Os}/^{188}\text{Os}$ values exceeds the analytical uncertainty. Thus, statistical recalculation, based on comparison of mean $^{187}\text{Os}/^{188}\text{Os}$ values with known dispersion, allows us to distinguish between two groups of detrital PGM at Bor-Uryah: (1) a mean value of 0.12400 ± 0.00015 , and the (2) mean value of 0.12561 ± 0.00025 (Table 5). The measured Os-isotope compositions for PGM from Guli and Bor-Uryah correspond to those suggested for the mantle and mantle peridotites, which have a relatively low $^{187}\text{Os}/^{186}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios as a result of evolution in a low Re/Os environment (among others, *Hattori and Hart, 1991; Luck and Allegre, 1991; Martin, 1991; Walker et al., 1996; Shirey and Walker, 1998; Brandon et al., 2000*).

Table 2. Selected electron microprobe (WDS) analyses of Os-rich alloys

Analyses	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample	H 3	B 7	GB 2-11 6c	GBB 5 6f	G 23-5 8d	G 1-12 8e	G 2-2 6b	B 2-29 6e	B 2-29 6e	B 2-29 6a	BU 1-4 6a	BU 1-4 6a	BU 1-8	BU 1-13
Mineral	Osmium	Osmium	Osmium	Osmium	Osmium	Os-Ir*	Os-Ir*	Os-Ir*	Os-Ir*	Os-Ir*	Os-Ir*	Os-Ir*	Osmium	Os-Ir*
wt. %														
S	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
As	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Fe	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,21	0,48	0,28	0,27	0,29	0,00	0,23
Ni	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cu	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Ru	0,00	1,64	2,50	2,51	2,93	3,60	3,73	6,08	5,53	2,53	2,94	2,27	0,38	2,69
Rh	0,00	0,00	0,00	0,00	0,00	0,63	0,39	0,69	1,40	0,35	0,34	0,00	0,00	0,00
Pd	0,00	0,00	0,00	0,00	0,33	0,46	0,21	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Os	99,91	93,24	86,73	85,65	82,81	80,10	62,18	54,47	29,59	62,88	63,33	68,26	88,66	62,40
Ir	0,00	4,55	11,41	11,80	14,31	12,43	33,93	37,24	51,52	33,81	32,67	29,46	10,98	34,22
Pt	0,00	0,39	0,00	0,00	0,00	2,20	0,36	0,37	10,08	0,00	0,00	0,00	0,00	0,00
Total	99,91	99,82	100,64	99,96	100,38	99,42	100,80	99,06	98,60	99,85	99,55	100,28	100,02	99,54
at. %														
S	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
As	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Fe	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,68	1,56	0,93	0,90	0,96	0,00	0,77
Ni	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cu	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Ru	0,00	3,05	4,58	4,63	5,35	6,56	6,74	10,89	9,91	4,64	5,39	4,16	0,71	4,96
Rh	0,00	0,00	0,00	0,00	0,00	1,13	0,68	1,21	2,47	0,63	0,61	0,00	0,00	0,00
Pd	0,00	0,00	0,00	0,00	0,57	0,80	0,36	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Os	100,00	92,13	84,43	83,93	80,34	77,53	59,66	51,82	28,17	61,23	61,65	66,48	88,45	61,11
Ir	0,00	4,45	10,99	11,44	13,74	11,90	32,22	35,06	48,54	32,58	31,47	28,39	10,84	33,16
Pt	0,00	0,38	0,00	0,00	0,00	2,08	0,34	0,34	9,36	0,00	0,00	0,00	0,00	0,00

Analyses 1–9 from Guli, 10–14 from Bor-Uryah; numbers 3–11 refer to analysis points on Figs. 6 and 8; * abbreviations of PGM: Os–Ir–Os–Ir alloy; Ir–Os Ir–Os alloy

Table 3. Selected electron microprobe (WDS) analyses of laurite–erlichmanite series from Guli

Analyses	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Sample	G 2-2	GB 2-11	GB 2-11	GBB 5	GBB 5	B 2-29	G 23-5 8c	G 23-5 8c	G 23-5 8c	G 23-5 8c	B 7	B 1	B 1	H 1	B 9
Figure	6b	6d	6d	6f	6f	6e	8c	8c	8c	8c	B 7	B 1	B 1	H 1	B 9
Mineral	Laurite	Laurite	ERL I*	Laurite	ERL II**	Laurite	Laurite	Laurite	Laurite	Laurite	ERL I*	Laurite	ERL I*	ERL II*	ERL II*
wt. %															
S	37,19	35,10	26,47	33,35	28,40	32,86	37,28	34,87	33,26	36,45	26,53	32,35	24,89	29,16	26,76
As	0,00	0,00	0,91	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,25	0,00	0,45	0,00	0,00
Fe	0,00	0,00	1,81	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,95	0,00	0,36	0,00	0,00
Ni	0,00	0,00	0,31	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cu	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Ru	52,11	44,52	1,66	38,19	11,09	36,53	54,24	42,43	35,92	52,24	0,85	34,44	0,35	17,52	5,48
Rh	1,29	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,14	0,00
Pd	0,92	0,68	0,33	0,57	0,12	0,40	0,00	0,36	0,30	0,00	0,00	0,00	0,00	0,39	0,00
Os	5,43	15,96	59,45	23,98	56,18	20,84	6,04	19,09	27,00	10,12	65,44	26,37	42,37	47,56	60,09
Ir	1,83	2,53	8,29	2,46	5,02	8,89	1,52	2,43	3,28	1,35	5,74	6,80	30,19	3,97	8,66
Pt	0,00	0,00	0,00	0,00	0,00	0,00	0,17	0,00	0,16	0,25	0,31	0,14	0,20	0,00	0,33
Total	98,77	98,79	99,23	98,55	100,81	99,52	99,25	99,18	99,92	100,41	100,07	100,10	98,81	99,74	101,32
at. %															
S	66,86	66,81	66,01	66,58	67,20	66,30	66,83	66,98	66,69	66,29	67,18	66,19	66,17	66,47	66,69
As	0,00	0,00	0,97	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,27	0,00	0,51	0,00	0,00
Fe	0,00	0,00	2,59	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,38	0,00	0,55	0,00	0,00
Ni	0,00	0,00	0,42	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cu	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Ru	29,72	26,88	1,31	24,19	8,32	23,38	30,84	25,85	22,85	30,13	0,68	22,35	0,30	12,67	4,33
Rh	0,72	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,81	0,00
Pd	0,50	0,39	0,25	0,34	0,09	0,24	0,00	0,21	0,18	0,00	0,00	0,00	0,00	0,27	0,00
Os	1,65	5,12	25,00	8,07	22,41	7,09	1,83	6,18	9,13	3,10	27,94	9,09	18,99	18,27	25,24
Ir	0,55	0,80	3,45	0,82	1,98	2,99	0,45	0,78	1,10	0,41	2,42	2,32	13,39	1,51	3,60
Pt	0,00	0,00	0,00	0,00	0,00	0,00	0,05	0,00	0,05	0,07	0,13	0,05	0,09	0,00	0,14
Ru number	95	84	4	75	27	77	94	81	71	91	2	71	2	41	15

Analyses 15–23 refer to laurite-erlichmanite intergrown with Os-rich alloys, analyses 24–29 correspond to PGM inclusions in Os-rich alloys. Numbers 15–23 refer to analysis points on Figs. 6 and 8; * abbreviations of PGM: *ERL I* erlichmanite showing uncommon Os for Ir substitution; *ERL II* erlichmanite with common Os for Ru substitution; Ru number = $[100^*Ru/(Ru + Os)]$

Table 4. Selected electron microprobe analyses (wt.%) of silicates and oxide inclusions in osmium nuggets

Number	1	2	3	4	5	6	7	8	9	10	11
Sample	B 4	B 6	A 6	A 25	B 5	B 4/1	B 4/1	B 4/1	B 4/2	B 4/2	B 4/2
Mineral	Ol-1	Ol-1	Crt	Crt	Mgt	Ol-2	Cpx	Sil-1	Sil-2	Sil-1	Cpx
SiO ₂	40.70	40.45	0.00	0.00	0.00	36.57	52.19	39.88	48.22	36.14	52.34
TiO ₂	0.03	0.00	1.87	3.57	0.00	0.05	0.94	1.70	1.80	3.10	0.70
Al ₂ O ₃	0.05	0.01	12.16	6.34	0.03	0.31	0.86	12.14	4.56	12.03	0.86
Cr ₂ O ₃	0.00	0.00	41.45	45.49	0.00	0.02	0.09	0.08	0.03	0.20	0.02
FeO	7.79	8.96	21.82	21.52	28.28	29.62	4.96	7.88	10.46	13.55	5.64
Fe ₂ O ₃	–	–	12.73	13.29	67.12	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.29	0.22	0.56	0.27	0.96	0.72	0.08	0.03	0.15	0.14	0.25
MgO	49.01	47.70	8.35	9.30	0.54	30.81	14.28	21.73	15.62	15.82	13.92
CaO	0.21	0.43	0.00	0.00	0.00	0.08	22.90	0.13	7.48	0.08	23.19
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	1.09	2.33	6.12	1.03	1.22
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.49	0.19	8.24	0.00
NiO	0.20	0.39	0.30	0.27	0.00	0.05	0.00	0.14	0.09	0.16	0.00
Total	98.28	98.16	99.24	100.05	96.93	98.23	97.39	92.53	94.72	90.49	98.14

Minerals from monophase (1–5) and polyphase (6–11) inclusions. *Ol-1* forsterite, *Crt* chromite, *Mgt* magnetite, *Ol-2* olivine, *Cpx* diopside, *Sil-1* silicate glass (?) enriched in K, *Sil-2* silicate glass (?) enriched in Na. FeO and Fe₂O₃ were calculated on the basis of charge balance

Since the ¹⁸⁷Os/¹⁸⁸Os values in all analyzed PGM do not exceed the value of the contemporary undifferentiated mantle material (CHUR) (0.12736 ± 0.00016) (Yin et al., 1996), a model Re–Os age can be calculated (method of Allegre and Luck, 1980). The Re/Os ratio of the Earth as a whole (i.e. Bulk Earth) and, in particular the mantle, has not changed during the 4.56 Ga of geological history. This permits the assumption that model Re/Os ages for mantle derivatives are close to the time of their formation. This is particularly true for Os-rich mantle minerals, as their ages cannot be underestimated. Overestimation of ages is also unlikely, since the Re–Os isotope system at the mineral level is well protected against crustal contamination. This phenomenon has been demonstrated for detrital 3.0–4.0 Ga Os-rich alloys and gold from the Evander and Klerksdorp goldfields at Witwatersrand, South Africa (Malitch et al., 2000, 2001a; Kirk et al., 2001). For the calculation of model (mantle-derived) ages, the contemporary and primary ¹⁸⁷Os/¹⁸⁸Os ratios in the undifferentiated mantle reservoir are considered to be 0.12736 ± 0.00016 and 0.09600 ± 0.00035, respectively (Yin et al., 1996). Therefore, the equation for the model Os-isotope age according to Kostoyanov (1998) is: $T = \frac{0.12736 - ^{187}\text{Os}/^{188}\text{Os}}{0.006862} (\text{Ga})(1)$, where ¹⁸⁷Os/¹⁸⁸Os is the ratio measured in the sample.

According to formula (1), the mean value of the Os-isotope ratio of different PGM (e.g. Os-rich alloys and laurite) from the Guli massif yield the same model ¹⁸⁷Os/¹⁸⁸Os ages of 423 Ma, whereas Os-rich alloys from the first and second groups at Bor-Uryah yield mean model ages of 490 and 256 Ma, respectively (Table 5). Other ¹⁸⁷Os/¹⁸⁸Os values for the present day mantle, frequently used to calculate model ages, are 0.1270 (Shirey and Walker, 1998) and 0.1290 ± 0.0008 (Meisel et al., 2001). In case the latter estimate is used the model ages would be

Table 5. *In-situ* laser ablation MC-ICP-MS osmium isotope compositions of PGM from the Guli and Bor-Uryah massifs, the Maimecha-Kotui Province

Analysis	Locality, Figure	Sample	Mineral	$^{186}\text{Os}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	$\gamma_{\text{Os}(t=0)}$	T, Ga
Guli							
1	Fig. 8b; 8c	G 23-5	Laurite ¹	0.11974 ± 0.00026	0.12439 ± 0.00027	-2,34	0,434
2	Fig. 8c	G 23-5	Laurite ¹	0.11989 ± 0.00029	0.12432 ± 0.00029	-2,39	0,444
3		G 23-5	Laurite ²	0.11991 ± 0.00008	0.12445 ± 0.00007	-2,28	0,424
4		G 23-5	Laurite ²	0.11993 ± 0.00009	0.12449 ± 0.00015	-2,25	0,418
5	Fig. 8d	G 23-5	Osmium ¹	0.11979 ± 0.00031	0.12455 ± 0.00031	-2,21	0,409
6	Fig. 8d	G 23-5	Osmium ¹	0.11938 ± 0.00035	0.12472 ± 0.00034	-2,07	0,384
7		G 23-5	Osmium ¹	0.11975 ± 0.00022	0.12435 ± 0.00023	-2,38	0,441
8		G 23-5	Osmium ¹	0.12006 ± 0.00026	0.12440 ± 0.00026	-2,32	0,431
9		G 23-5	Osmium ¹	0.11979 ± 0.00011	0.12443 ± 0.00010	-2,30	0,427
10		G 2-2	Laurite ²	0.11984 ± 0.00005	0.12463 ± 0.00009	-2,14	0,398
11		G 2-2	(Os, Ir) ²	0.11971 ± 0.00013	0.12444 ± 0.00018	-2,29	0,426
12	Fig. 8e	G 1-12	(Os, Ir) ²	0.11989 ± 0.00020	0.12433 ± 0.00010	-2,37	0,441
Average			Laurite (n = 5)	0.11986 ± 0.00015	0.12446 ± 0.00015	-2,28	0,423
Average			Osmium (n = 7)	0.11978 ± 0.00023	0.12446 ± 0.00022	-2,28	0,423
Average			PGM (n = 12)	0.11981 ± 0.00020	0.12446 ± 0.00020	-2,28	0,423
Bor-Uryah							
13		BU 1-8	(Os, Ir) ²	0.11939 ± 0.00017	0.12403 ± 0.00016	-2,61	0,485
14		BU 1-9	Osmium ²	0.11986 ± 0.00009	0.12396 ± 0.00013	-2,67	0,495
Average			PGM Group I	0.11963 ± 0.00013	0.12400 ± 0.00015	-2,64	0,490
15		BU 1-4	(Os, Ir) ²	0.11961 ± 0.00027	0.12571 ± 0.00019	-1,30	0,240
16		BU 1-4	(Os, Ir) ²	0.11962 ± 0.00022	0.12562 ± 0.00032	-1,37	0,253
17		BU 1-4	(Os, Ir) ²	0.11949 ± 0.00033	0.12560 ± 0.00025	-1,38	0,256
18		BU 1-13	(Os, Ir) ²	0.11978 ± 0.00024	0.12551 ± 0.00024	-1,45	0,270
Average			PGM Group II	0.11963 ± 0.00027	0.12561 ± 0.00025	-1,38	0,256

(Os, Ir) iridian osmium; n number of analyses; ¹ and ² LA MC-ICP-MS analyses performed in March, 2001 and June, 2001, respectively. The parameter γ_{Os} is the percent deviation of the isotopic composition of a PGM compared with the average chondritic mantle composition at present: $\gamma_{\text{Os}} = ({}^{187}\text{Os}/{}^{188}\text{Os} \text{ sample} / 0.12736 - 1) \times 100$, where 0.12736 is a value of present day isotopic composition of the mantle reservoir (Yin et al., 1996)

Table 6. NTI-MS osmium isotope compositions of PGM from the Guli, Bor-Uryah, Kondyor and Inagli clinopyroxenite–dunite massifs, the Siberian Craton

Analysis	Locality, sample	Mineral	Atomic proportions	Os ¹⁸⁷ /Os ¹⁸⁸ **	$\gamma_{\text{Os}(t=0)}$	T, Ga
Guli:						
1	G 12	Osmium	Os _{0.94} Ir _{0.05} Ru _{0.01}	0.1247 ± 0.0002	– 2,09	0,388
2	GU 1-1	Osmium	Os _{0.98} Ir _{0.01} Ru _{0.01}	0.1247 ± 0.0003	– 2,09	0,388
3	GU 1-2	Osmium	Os _{0.98} Ir _{0.02}	0.1252 ± 0.0003	– 1,70	0,315
4	GU 1-3	Osmium	Os _{0.94} Ir _{0.04} Ru _{0.01} Pt _{0.01}	0.1251 ± 0.0003	– 1,77	0,329
5	GU 1-4	Osmium	Os _{0.81} Ir _{0.16} Ru _{0.02} Pt _{0.01}	0.1248 ± 0.0003	– 2,01	0,373
6	GU 1-5	Osmium	Os _{0.80} Ir _{0.15} Ru _{0.04} Pt _{0.01}	0.1247 ± 0.0003	– 2,09	0,388
7	GU 1-6	Osmium	Os _{0.80} Ir _{0.16} Ru _{0.04}	0.1246 ± 0.0003	– 2,17	0,402
8	GU 1-7	Os–Ir alloy	Os _{0.76} Ir _{0.22} Ru _{0.02}	0.1251 ± 0.0003	– 1,77	0,329
9	GU 1-8	Os–Ir alloy	Os _{0.75} Ir _{0.23} Ru _{0.02}	0.1247 ± 0.0003	– 2,09	0,388
10	GU 1-9	Os–Ir alloy	Os _{0.74} Ir _{0.21} Ru _{0.04} Pt _{0.01}	0.1248 ± 0.0002	– 2,01	0,373
Average		Alloys (n = 10)		0.1248 ± 0.0003	– 2,01	0,373
Bor-Uryah:						
11	BU 1-9	Osmium	Os _{0.89} Ir _{0.11}	0.1240 ± 0.0002	– 2,64	0,490
12	BU 1-7	Os–Ir alloy	Os _{0.63} Ir _{0.33} Ru _{0.04}	0.1257 ± 0.0003	– 1,30	0,242
Kondyor:						
13	K 13	Osmium*	Os _{0.96} Ir _{0.03} Ru _{0.01}	0.1248 ± 0.0003	– 2,01	0,373
14	K 14	Osmium*	Os _{0.93} Ir _{0.05} Ru _{0.01} Pt _{0.01}	0.1252 ± 0.0003	– 1,70	0,315
15	K 15	Osmium	Os _{0.90} Ir _{0.06} Ru _{0.02} Pt _{0.02}	0.1252 ± 0.0003	– 1,70	0,315
16	K 16	Osmium	Os _{0.86} Ir _{0.11} Ru _{0.02} Pt _{0.01}	0.1248 ± 0.0003	– 2,01	0,373
17	K 17	Os–Ir alloy	Os _{0.73} Ir _{0.19} Ru _{0.07} Pt _{0.01}	0.1252 ± 0.0003	– 1,70	0,315
Average		Alloys (n = 5)		0.1250 ± 0.0003	– 1,85	0,344
Inagli:						
18	I 4	Ir–Os alloy	Ir _{0.56} Os _{0.16} Pt _{0.12} Ru _{0.11} Rh _{0.05}	0.1250 ± 0.0003	– 1,85	0,344
19	I 6	Osmium	Os _{0.83} Ir _{0.12} Ru _{0.04} Pt _{0.01}	0.1249 ± 0.0003	– 1,93	0,358
20	I 7	Osmium	Os _{0.80} Ir _{0.12} Ru _{0.05} Pt _{0.03}	0.1249 ± 0.0003	– 1,93	0,358
Average		Alloys (n = 3)		0.1249 ± 0.0003	– 1,90	0,353

PGM from Guli and Bor-Uryah are solitary Os-rich alloy nuggets, whereas PGM from Kondyor and Inagli are Pt–Fe alloy grains containing minor amounts of Os-rich alloys. PGM are from: (1) the chromitites (*) and (2) placers. ** - normalized after $^{190}\text{Os}/^{188}\text{Os} = 1.98379$ (Tuttas, 1992). T calculated model ages with respect to data by Yin et al. (1996). Analyses 2–10 after Malitch (1999), 13–20 after Malitch et al. (2001c)

approximately 0.30 Ga older. However, as evidenced by recent studies on base metal sulphides (Alard et al., 2001a, b) ultramafic xenoliths cannot be considered a valid proxy material in respect of PGE-mineralization.

Discussion

Os-rich minerals and PGE- specialization of source rocks

The derivation of the Os-rich nuggets investigated at Guli and Bor-Uryah is obvious: the placer deposits display close spatial association with the

ultramafic massifs. Furthermore, primary PGM from dunite and chromitite at Guli (*Balmasova et al.*, 1992; *Malitch and Rudashevsky*, 1992; *Malitch*, 1999) share mineralogical and compositional characteristics with the detrital PGM.

Dominance of Os-rich alloys over Pt–Fe alloys is not unusual in ultramafic complexes. In fact, it is considered a typical feature of PGE-occurrences in Alpine-type (or ophiolite-type) dunite–harzburgite complexes worldwide (*Stumpfl*, 1974; *Cabri and Harris*, 1975; *Legendre and Auge*, 1986; *Auge and Johan*, 1988; *Melcher et al.*, 1994; *Palandzhian et al.*, 1994; *Cabri et al.*, 1996; *Auge et al.*, 1998; etc.). However, the Guli massif, which is mainly composed of dunite, wehrlite and clinopyroxenite, shows high PGE-metallogenic potential. This is in contrast to Alpine-type ultramafic complexes. The predicted reserves (about 15 metric tons) of the iridium–osmium placer from the Ingarinda River and a number of other placer deposits of the Maimecha-Kotui Province make them comparable to the economically significant Witwatersrand deposits, South Africa.

The Guli clinopyroxenite–dunite massif, like other clinopyroxenite–dunite complexes, e.g. such as Kondyor and Inagli (*Malitch*, 1991, 1999), is situated at the periphery of the Siberian Craton, rather than within an extensive belt at convergent plate margins, which is typical for ophiolite-type complexes. Furthermore, in the Guli massif, solitary osmium minerals (Fig. 5), which are the most abundant PGM, are compositionally compatible with Os–Ir and Ir–Os inclusions in Pt–Fe alloys from zoned ultramafic complexes (e.g., *Nixon et al.*, 1990; *Cabri et al.*, 1996; *Malitch and Thalhammer*, 2002). In contrast, the composition of Ru–Os sulphides (Fig. 7B) from the Os-rich nuggets investigated is compatible with the wide compositional range of the laurite–erlichmanite series of the mantle-hosted ophiolitic chromitite at Kempirsai (*Melcher et al.*, 1997; *Garuti et al.*, 1999) and Kraubath (*Malitch et al.*, in press). Ru-dominant laurite inclusions from chromitite at Guli (*Malitch*, 1999) are close to those of chromitites from the Semail and Vourinos ophiolitic complexes (*Legendre and Auge*, 1986; *Auge and Johan*, 1988). Ru–Os sulphides from Guli are, thus, generally similar to the A and D trends, as defined by *Garuti et al.* (1999) for mantle-hosted chromitites.

The set of PGM documented in dunite and chromitite of the Guli massif and related placers corresponds in general to that from placers associated with zoned clinopyroxenite–dunite massifs (*Malitch et al.*, 1995; *Cabri et al.*, 1996; *Malitch and Lopatin*, 1997b; *Malitch*, 1999). Furthermore, the broad spectrum of inclusions present within osmium minerals is comparable to that found in alluvial Pt–Fe alloys, which are associated with zoned platiniferous ultramafic complexes (Uralian- or Alaskan-type and Aldan-type intrusions) (*Rudashevsky et al.*, 1982; *Nixon et al.*, 1990; *Auge and Legendre*, 1992; etc.). However, the unusual diversity of Ru–Os sulphides and predominance of Os–(Ir–Ru) over Pt–Fe alloys in the placers at Guli, Maimecha-Kotui Province, differs from PGM from zoned ultramafic massifs, and thus underlines the uniqueness of the iridium–osmium speciation of these placers.

The Guli massif shows intermediate features between typical zoned- and ophiolite-type ultramafic complexes. In spite of its large area and specialization for refractory PGE, Guli has more similarities with zoned platiniferous clinopyroxenite–dunite complexes rather than with ophiolitic dunite–harzburgite complexes.

Mineralogical constraints for genesis of PGE-mineralisation

Most of the nuggets studied are homogeneous Os-rich alloys, with a large variation in composition (e.g., Os–Ir–(Ru) substitution) from one nugget to another. Texturally, most nuggets appear to be aggregates of crystals with the same composition (Figs. 4, 6a). This implies that the segregation of crystals is not a late phenomenon but is contemporaneous with original mineralization.

The formation of Os-rich minerals, in close association with ultramafic rocks at Guli, is proved by presence of numerous inclusions and intergrowths of chromite, olivine and clinopyroxene in detrital osmium (Fig. 6; Table 4), and the presence of *in-situ* Os alloy in olivine from dunite (Balmasova et al., 1992) and Os–Ir alloy and laurite in chromite from chromitite (Malitch, 1999). Both Os–Ir–Ru and Pt–Fe alloys, and traces of laurite form at a very early stage of magmatic differentiation under low sulphur fugacities, high-temperature conditions and, most likely, in the presence of a fluid phase, according to experimental results and natural observations (e.g., Bird and Bassett, 1980; Fleet and Stone, 1991; Nakagawa and Franko, 1997; Amosse et al., 2000; Brenan and Andrews, 2001). The presence of Ru–Os, Os–Ir and base-metal sulphides in the Os-rich alloys suggests that the condition of the formation for those minerals was close to PGE alloy – PGE sulphide equilibrium.

Equilibrium phase relations of Os-rich alloys at Guli and Bor-Uryah, based on the binary system Os–Ir (Massalski, 1993), and presence of exsolution lamellae of polycomponent Ru–Os-rich alloys in detrital ferroan platinum at Guli (Badanina and Malitch, 1998; Malitch and Badanina, 1998; Malitch and Thalhammer, 2002) are indicative of high-temperature origin of PGM. Taking into account that platinum forms limited isomorphous mixtures with refractory PGE, the discovery of natural polycomponent solid solutions of the Ru–Os–Ir–Pt–Fe system (Malitch and Badanina, 1998) points to a very specific set of geodynamic conditions at the time of formation and emplacement of the ultramafic host substrate. The nature of the above mentioned PGM paragenesis, which originated at high but stable P-T conditions, is indicative of the formation of ultramafic rocks at considerable depths. Compositionally similar detrital 3.0–4.0 Ga polycomponent PGE-alloys, derived from an enigmatic primary source, were found in the Archean paleoplacers of the Witwatersrand Basin (Malitch et al., 2000, 2001a).

Os-isotopic constraints for genesis of PGE-mineralization

The early formation of Os-rich minerals at high temperatures implies that the Os-isotopic composition of Os-rich alloys and Ru–Os sulphides should reflect that of the source region. Therefore, the low $^{187}\text{Os}/^{188}\text{Os}$ values obtained, corresponding to Os-isotopic composition of the mantle, and the constant Os-isotope ratios of different PGM at Guli, clearly indicate a common chondritic or subchondritic mantle source for the PGE.

The $^{187}\text{Os}/^{188}\text{Os}$ for the PGM nuggets at Guli and the second group at Bor-Uryah are close to those from our former NTI-MS study, which showed mean values of 0.1248 ± 0.0003 and 0.1257 ± 0.0003 , respectively (Malitch and Kostoyanov, 1999). The very narrow range of $^{187}\text{Os}/^{188}\text{Os}$ values of PGM at Guli, exemplified by both LA MC-ICP-MS and NTI-MS (0.12446 ± 0.00020 and

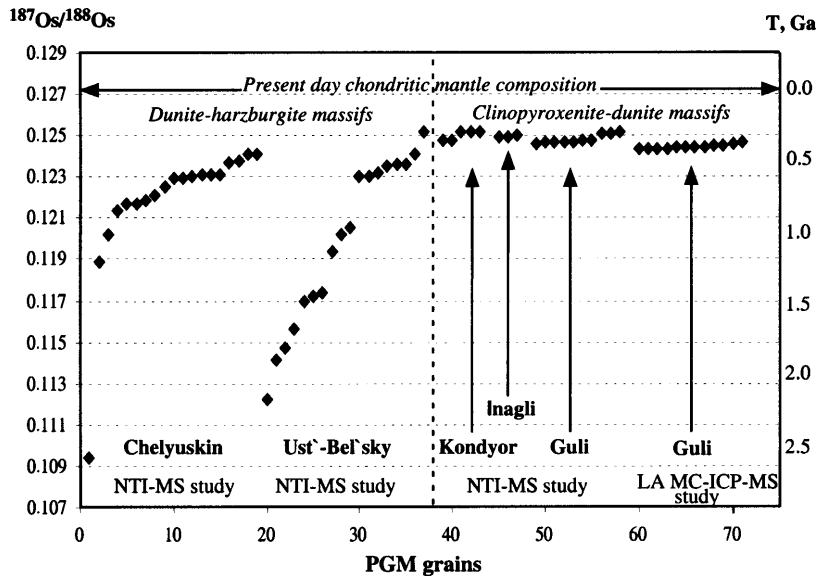


Fig. 9. Os-isotopic composition of PGM from dunite–harzburgite and clinopyroxenite–dunite complexes, Russia. NTI-MS data are from *Malitch et al. (2002)* for Chelyuskin PGM, from *Rudashevsky et al. (1999)* for Ust'-Bel'sky PGM, from *Malitch (1999)* for Guli PGM, and from *Malitch et al. (2001c)* for Kondyor and Inagli PGM

0.1248 ± 0.0003 respectively, the expanding uncertainties correspond to the 95%-confidence interval, Tables 5 and 6), is consistent with similar results for PGM from Kondyor and Inagli (Table 6; Fig. 9) and likely indicates a highly productive single-stage PGM formation in clinopyroxenite–dunite complexes. The ore-forming system, invariably related to dunites, was driven by mantle-derived fluids. This resulted in the mobilization and concentration of chromite and PGE in the upper parts of the dunite bodies during their ascent in a semi-ductile state (*Malitch, 1995, 1998*). This hypothesis could explain the fact that upper parts of the massifs are enriched in chromitites, representing the most important PGE source for platinum placers. We, therefore, propose that the PGE were derived from the mantle without any significant contribution of crustal Os, and that the $^{187}\text{Os}/^{188}\text{Os}$ values have not been changed by subsequent processes (e.g. transport, sedimentation and weathering during placer formation).

The $^{187}\text{Os}/^{188}\text{Os}$ values of the PGM nuggets investigated are close to those derived from zoned and ophiolitic ultramafic complexes worldwide (*Hattori and Hart, 1991; Hattori and Cabri, 1992; Borg and Hattori, 1997; Hirata et al., 1998; Bird et al., 1999; Malitch et al., 2001c, 2002*). However, the range of $^{187}\text{Os}/^{188}\text{Os}$ and the γOs values in PGM derived from clinopyroxenite–dunite complexes are distinctly different from those observed for Alpine-type ultramafic complexes. For instance, PGM derived from the Guli, Kondyor and Inagli complexes, Siberian Craton, Russia show a narrow range of $^{187}\text{Os}/^{188}\text{Os}$ and γOs values (e.g., 0.12432–0.12520 and from -2.39 to -1.70 , respectively, $n = 30$, Tables 5 and 6, Fig. 9), whereas those from the Chelyuskin Complex, Taimyr, Russia, the Ust'-Bel'sky Complex, Far East, Russia (Fig. 9) and the bedrock PGM from the Speik Complex, Eastern Alps, Austria (unpublished data), have a wide range of $^{187}\text{Os}/^{188}\text{Os}$ (e.g.

0.1094–0.1252, $n = 55$) and γOs values (e.g. from -14.10 to -1.70 , $n = 55$). It is, also, noteworthy, that $^{187}\text{Os}/^{188}\text{Os}$ values of Ru–Os sulphides and sulpharsenides from podiform chromitites at Kraubath and Hochgrössen, Speik Complex (0.1158–0.1239, $n = 19$, NTI-MS and LA MC-ICP-MS study; unpublished data) are almost identical to those of detrital Os-rich alloys derived from other Alpine-type ultramafic massifs (Fig. 9), which correspond to chondritic or subchondritic $^{187}\text{Os}/^{188}\text{Os}$ values of the upper mantle residual rocks. These results are consistent with a model, involving a prolonged melting-event history of parent ultramafic protoliths in the mantle, but which did not result in a significant concentration of PGE. In contrast, a highly productive single stage process of PGE-concentration in clinopyroxenite–dunite complexes [deduced from almost identical Os-isotopic composition of PGM (Fig. 9)], is in accordance with a significant metallogenic potential of their parent ultramafic protoliths.

On the basis of the Os-isotopic data obtained, we conclude that the Os-isotopic composition for PGM nuggets derived from placer deposits, with an unknown provenance, could be employed as a useful tool in deciphering their parent bed-rock sources (e.g., dunite–harzburgite and clinopyroxenite–dunite ultramafic complexes). Further work, combined with previously unpublished data, will explore this application in depth.

Os-isotopic constraints for timing of PGE-mineralization and geodynamic implications

A re-assessment of the metallogenic potential of the entire Maimecha-Kotui province, as part of the northern portion of the Siberian Craton, is given by Malitch et al. (1996). The area has previously been evaluated as prospective for apatite, phlogopite, iron, nepheline, rare metals and rare earth elements (REE) associated with the Late Triassic ijolite–carbonatite complexes (e.g., Egorov, 1991; Kogarko et al., 1995, among others). On the basis of geological, mineralogical and geochemical studies, Malitch and Lopatin (1997a, b) proposed a distinct origin for the ultramafic and alkaline rock suites of the Guli massif and, thus, distinguished between the Guli clinopyroxenite–dunite and the Maimecha-Kotui ijolite–carbonatite complexes. Os-isotope model ages of 370–420 Ma for the Guli clinopyroxenite–dunite complex correspond to a Middle Paleozoic (S_1 – D_3) formation age. Consequently, the ultramafic complex is older than the spatially-associated alkaline suite (i.e., part of the Late Triassic Maimecha-Kotui Complex). This evidence indicates that they are genetically distinct.

Os-isotopic data from this study are consistent with previous whole rock and mineral Os-isotopic studies (e.g., Parkinson et al., 1998; Snow and Schmidt, 1999; Brandon et al., 2000; Fig. 9): Os-isotope systematics suggest that melt depletion event(s), recorded by ‘unradiogenic’ $^{187}\text{Os}/^{188}\text{Os}$, at Guli and certain other peridotite occurrences worldwide are older than the time of their emplacement to the crustal level. In this context, the Os-rich alloys at Bor-Uryah, that constitute the first group (i.e., $\gamma\text{Os} = -2.64$, $T = 490$ Ma), show the oldest model ages for the ultramafic protoliths at the Maimecha-Kotui Province, while the PGM from the second group (i.e., $\gamma\text{Os} = -1.38$, $T = 256$ Ma) are consistent with magmatic activity at Palaeozoic–Mesozoic boundary (Malitch, 1975; El’yanov and Andreev,

1991), which was responsible for the emplacement of intrusive bodies. These Middle Palaeozoic and Early Mesozoic events represent significant stages in the development of the Siberian Craton, characterized by upwelling of the mantle and repeated reactivation of deep, older mantle fractures to rift zones (*Malitch, 1975; Malitch, 1999*). Therefore, all clinopyroxenite–dunite massifs of the Siberian Craton are located in zones of long-term deep faults, which were initially created in the Proterozoic and repeatedly reactivated during younger rifting.

Conclusions

1. Osmium minerals [osmium Os and iridian osmium (Os, Ir)] constitute the majority of PGM in placers from the Maimecha-Kotui Province. The compositional changes of the osmium-rich alloys are mainly due to Os-for-Ir and Os-for-Ru substitution. The primary origin of investigated PGM, in close association with ultramafic rocks (chromitite, dunite, clinopyroxenite) of the Guli massif, is proved by the existence of numerous inclusions of chromite, olivine and clinopyroxene in osmium minerals.
2. The ultramafic rock assemblage of dunite, chromitite, wehrlite and clinopyroxenite at Guli, and its significant potential for placer formation coincide well with typical zoned massifs of Uralian-, Alaskan- and Aldan-type; whereas the large size of the ultramafic complex, its shape, the lack of a concentrically zoned structure, and the common occurrence of refractory Os–Ir–(Ru) alloys matches with ophiolitic massifs. The considerable resources of osmium in the placer deposits, associated with the Guli massif, are considered to represent the main Os source in Russia.
3. Subchondritic Os-isotopic composition of different Os-rich minerals, with a very narrow range of $^{187}\text{Os}/^{188}\text{Os}$ and γOs values at Guli (from 0.12432 to 0.12472 and from -2.39 to -2.07 , respectively), is consistent with a highly productive single stage formation of PGM. Os-isotope model ages of distinct PGM at Guli indicate that this event took place in the Middle Paleozoic, prior to the Devonian–Carboniferous boundary, which corresponds to a stage of active tectonism in the development of the Siberian Craton. Low $^{187}\text{Os}/^{188}\text{Os}$ and γOs values of PGM at Bor-Uryah form two groups, thus, implying two events of PGE concentration and PGM formation during the evolution of the Bor-Uryah massif.
4. The Os-isotope results show that the Re–Os system, represented by PGM, remained unchanged from the time of formation of the PGM until now. This supports the conclusion that placer PGM are primary in origin, and are not the result of authigenic growth during river transport. On the basis of the present Os-isotope data, we propose that the range of $^{187}\text{Os}/^{188}\text{Os}$ values in detrital PGM of unknown source could be used to distinguish different ultramafic sources (e.g., dunite–harzburgite and clinopyroxenite–dunite complexes).

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