# Pt-Fe NUGGETS DERIVED FROM CLINOPYROXENITE-DUNITE MASSIFS, RUSSIA: A STRUCTURAL, COMPOSITIONAL AND OSMIUM-ISOTOPE STUDY

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#### Abstract

Combined structural, compositional and osmium-isotope data on selected Pt-Fe nuggets from economically important placer deposits closely linked to clinopyroxenite-dunite massifs of the Siberian Platform (Kondyor, Inagli, Guli) and the Middle Urals (Nizhny Tagil), Russia, are presented for the first time. Pt-Fe alloys investigated are *ferroan platinum* (space group *Fm3m*) with a composition close to Pt<sub>3</sub>Fe. This emphasizes the necessity of an X-ray study in identifying the particular Pt-Fe alloy species. Less common are compositions such as Pt<sub>2</sub>Fe and an intimate intergrowth of Pt<sub>3</sub>Fe<sub>2</sub> and PtFe. Other platinum-group minerals (PGM) observed in *ferroan platinum* include a diversity of Os-Ir-Ru alloys, PGE sulfides [laurite, malanite, cuproiridsite, cooperite, and an unnamed base metal - (Ir,Pt) monosulfide], PGE sulfarsenides (hollingworthite, irarsite), Pt-Pd tellurides (moncheite, telluropalladinite) and stibiopalladinite. This suite of PGM is consistent with those from other zoned or Uralian-Alaskan-type massifs. However, unusually Ru-rich alloys included in *ferroan platinum* of Guli are characteristic of PGM derived from an ophiolite source and underline the transitional signature of the Guli massif between zoned- and ophiolite-type complexes. Pd-rich ferroan platinum nuggets indicate a derivation from clinopyroxenite source-rock, whereas Ir-rich Pt-Fe alloys suggest a chromitite source. The presence of numerous Os-Ir-Ru exsolution lamellae in ferroan platinum are indicative of a hightemperature origin of the PGM. The first Os-isotope data from Os-rich minerals from chromitites and placers closely associated to the Kondyor and Inagli massifs reveal low <sup>187</sup>Os/<sup>188</sup>Os values with a very narrow range, indicative of a common mantle source of the PGE, implying that the PGM are of primary origin. Disintegration of parent ultramafic source-rocks and short-range mechanical transport of liberated PGM formed the placers. Os-isotope model ages in the range of 340 to 355 Ma constrain the formation age of the Kondyor and Inagli massifs of the Aldan Province at the southeastern part of the Siberian Craton, and closely match those from the Guli massif (370 Ma) of the Maimecha-Kotui Province at the northern part of the Siberian Craton.

Keywords: ferroan platinum, Os-Ir-Ru alloys, chromitite, clinopyroxenite-dunite massif, placer, Urals, Siberian Craton, Russia.

#### Sommaire

Nous présentons, pour la première fois, une description structurale, minéralogique et isotopique d'une collection de pépites de Pt–Fe provenant de gisements de type placer d'intérêt économique, étroitement liés aux massifs de clinopyroxénite–dunite de la platteforme sibérienne (Kondyor, Inagli, Guli) et du centre de la chaîne des Ourales (Nizhny Tagil), en Russie. Les alliages Pt–Fe comprennent des exemples de platine ferreux (groupe spatial *Fm3m*), ayant une composition proche de Pt<sub>3</sub>Fe. Nos résultats soulignent l'importance de données de diffraction X dans l'identification des espèces d'alliage Pt–Fe. Moins courantes sont les compositions telles Pt<sub>2</sub>Fe et une intercroissance intime de Pt<sub>3</sub>Fe<sub>2</sub> et PtFe. Parmi les autres minéraux du groupe du platine inclus dans le platine ferreux, on trouve une variété d'alliage Os–Ir–Ru, des sulfures des éléments du groupe du platine (EGP) [laurite, malanite, cupro-iridsite, cooperite, et un monosulfure contenant métaux de base et (Ir,Pt) sans nom], les sulfarséniures hollingworthite et irarsite, des tellurures de Pt–Pd (monchéite, telluropalladinite) et stibiopalladinite. Cette suite de minéraux des EGP ressemble à celles d'autres massifs zonés de type Ourale–Alaska. Toutefois, à Guli, nous trouvons des alliages inhabituels riches en Ru dans le platine ferreux; ils sont plutôt caractéristiques d'une source ophiolitique et soulignent le caractère transitionnel du massif de Guli, entre un massif zoné et un massif à caractère ophiolitique. Les pépites de platine ferreux riches en palladium seraient dérivées d'un socle clinopyroxénitie, tandis que les alliages Pt–Fe riches en Ir auraient été dérivés de chromitites. La présence de nombreuses lamelles d'exsolution Os–Ir–Ru dans le platine ferreux indiquent la formation de la suite à température

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élevée. Les premières données sur le système isotopique de l'osmium dans les minéraux provenant de chromitites et de placers étroitement associés aux complexes de Kondyor et d'Inagli révèlent de faibles valeurs du rapport <sup>187</sup>Os/<sup>188</sup>Os, avec un écart très étroit, indication d'une source des EGP dans le manteau, et donc du caractère primaire des pépites. La désintégration de socles ultramafiques et un transport mécanique sur de courtes distances rendent compte des placers. Les âges calculés selon les rapports d'isotopes d'osmium, dans l'intervalle de 340 à 355 Ma, montrent que la formation des massifs de Kondyor et d'Inagli dans la Province d'Aldan, dans le secteur sud-est du craton sibérien, concordent bien avec l'âge de mise en place du pluton de Guli (370 Ma) dans la Province de Maimecha–Kotui, dans la partie nord du même craton.

(Traduit par la Rédaction)

Mots-clés: platine ferreux, alliages Os-Ir-Ru, chromitite, massif de clinopyroxénite-dunite, placer, Ourales, craton sibérien, Russie.

### INTRODUCTION

Placer deposits containing platinum-group minerals (PGM), particularly Pt-Fe alloys, were the principal world producer of platinum-group elements (PGE) until the beginning of the 20th century, when platinum was first discovered in the Bushveld Complex (Schneiderhöhn 1929). The majority of placer mining was then carried out in Russia, particularly in the Urals (e.g., Duparc & Tikhonowitch 1920, Vysotzkiy 1925, Betekhtin 1961). Over a period of about 180 years, mining operations yielded about 330 tonnes of platinum (Barannikov & Volchenko 1997). These deposits, once the largest PGE deposits in the world, are closely linked to mafic-ultramafic massifs that are located in elongate tectonic belts, developed at convergent plate margins, and termed zoned-type or Alaskan-type massifs (Taylor & Noble 1960, Naldrett & Cabri 1976, Nixon et al. 1990, Johan et al. 1991, Hattori & Hart 1991, Tistl 1994, Cabri et al. 1996) or Uralian-Alaskan-type massifs (Foley et al. 1997, Garuti et al. 1997) in the western literature. In Russia, however, massifs located within similar tectonic settings are known as of Uralian-type (e.g., Nizhny Tagil, Kytlym, Gal'moenan, etc.), but massifs situated in the periphery of stable cratons (e.g., the Siberian Craton) are termed Aldan-type or zonedtype massifs (e.g., Kondyor, Inagli, Chad, etc.; Rozhkov et al. 1962, Efimov & Efimova 1967, Razin 1976, Efimov & Tavrin 1978, Efimov 1984, 1998, El'yanov & Andreev 1991, Lazarenkov et al. 1992, Nekrasov et al. 1994, Malitch 1999). In spite of the fact that the main platinum placer deposits in the Urals are nearly mined out, placers are still the second most important Pt producer in Russia, after the Cu-Ni sulfide ores of Noril'sktype intrusions. The total platinum recovery from placer deposits in the Aldan Province (e.g., Kondyor and Inagli) in the southeastern part of the Siberian Craton, and from the Korvak Province (e.g., Gal'moenan and Seinav) in Far-Eastern Russia, reached in recent times about one-third of the annual production of platinum in Russia (Zaitsev et al. 1998, Cowley & Matthey 1999, Malitch 1999).

The principal PGM occurring in placers associated with zoned ultramafic massifs are Pt–Fe alloys, followed by Os–Ir–Ru–Pt alloys, although a great variety of other subordinate PGM have been identified lately (e.g., Toma & Murphy 1977, Cabri et al. 1981, Rudashevsky 1989, Nixon et al. 1990, Cabri & Genkin 1991, Mochalov et al. 1991, Slansky et al. 1991, Evstigneeva et al. 1992, Nekrasov et al. 1994, Cabri et al. 1996, Tolstykh & Krivenko 1997, Mochalov & Khoroshilova 1998, among others). Protracted confusion over the classification and nomenclature of Pt-Fe alloys was resolved by the suggestions of Cabri & Feather (1975). However, owing to the wide compositional range of mineral phases in the systems Pt-Fe and Pt-Fe-Cu (i.e., Cabri et al. 1973, Shahmiri et al. 1985), incorrect use of the nomenclature of Cabri & Feather (1975) has continued. Bowles (1990), for instance, refers to the nomenclature of Cabri & Feather (1975), but chooses to ignore the existence of *ferroan platinum*. a variety of Pt-Fe alloy with a face-centered cubic structure (fcc) and a Fe-content between 20 and 50 at.% according to Cabri & Feather (1975). Clear identification of the particular mineral species in the system Pt-Fe by X-ray studies is based on the degree of order in the structure, whereby a face-centered cubic, primitive cubic, or tetragonal structure can be distinguished. However, X-ray powder-diffraction data do not always prove the mineral identity unequivocally because ordering reactions may occur during mechanical treatment of alloys (*i.e.*, preparation of sample for X-ray analysis). Furthermore, Pt-Fe alloy is commonly designated isoferro*platinum* both in the western and particularly in the eastern literature, although X-ray data are lacking (e.g., Toma & Murphy 1977, Johan et al. 1991, Mochalov et al. 1991, Slansky et al. 1991, Augé & Legendre 1992, Rudashevsky et al. 1992a, b, Nekrasov et al. 1994, Palandzhian et al. 1994, Tolstykh & Krivenko 1997, Mochalov & Khoroshilova 1998, Augé et al. 1998, Ohnenstetter et al. 1999). The latter comment applies, in our opinion, to Pt-Fe alloy compositions close to Pt:Fe = 1, which are commonly referred to as *tetrafer*roplatinum. A further complication is the influence of small amounts of Ir, Os, Ru, Rh, Pd, as well as Cu and Ni on the structure of natural Pt-Fe alloys.

In this paper, we present the first results of a study of selected Pt–Fe nuggets from four economically important Russian placer deposits: Kondyor and Inagli (Aldan Province, eastern Siberian Craton), Guli (Maimecha–Kotui Province, northern part of the Siberian Craton), and Nizhny Tagil (Middle Urals). We direct particular emphasis to the structure and compositional characteristics of Pt–Fe alloys and the included Os–Ir–Ru alloy phases. On the basis of these results, we assess the similarities and differences among placers of the Siberian Craton and those of the Uraliantype Nizhny Tagil massif. Finally, we present the first osmium isotope data of osmium-rich minerals in order to focus on the origin of the PGM, the source of the PGE, and to place age constraints on the formation of the particular massifs.

# GEOLOGICAL SETTING AND SAMPLE LOCATION

The nuggets studied were derived from placer deposits closely associated with four clinopyroxenite-dunite complexes (Fig. 1). They are mainly composed of dunite and associated chromitite, metadunite, wehrlite and clinopyroxenite. The presence of PGE placers in spatial association with such ultramafic rocks is a specific feature of these massifs. Since the beginning of the sixties, increasing scientific interest has been devoted to these complexes. There have been a significant number of publications in Russian (Rozhkov et al. 1962, Malakhov & Malakhova 1970, Efimov 1984, Lazarenkov et al. 1992, Gurovitch et al. 1994, Nekrasov et al. 1994, Malitch 1999, and references cited therein) and lately also in the international literature (e.g., Razin 1976, Cabri & Genkin 1991, Efimov et al. 1993, Borg & Hattori 1997, Cabri & Laflamme 1997, Malitch 1998, Mochalov & Khoroshilova 1998, Okrugin 1998, among others).

The main geological characteristics of the four mafic–ultramafic complexes are presented below, with particular emphasis on Guli and Kondyor because (1) these are less known in the literature, and (2) the majority of the samples we investigated were taken from them.

### The Kondyor Massif

The Kondyor massif is situated in the southeastern part of the Siberian Craton (east of the Aldan Shield, Fig. 1a). The massif intrudes Archean basement and Late Proterozoic (Riphean) terrigenous-carbonaceous rocks of the Enninsk and Omninsk suites, forming a dome-like structure. The oval body is about 6 km in diameter, with a concentrically zoned structure mainly composed of dunite (Fo<sub>90-95</sub>), which forms the central part of the massif (Fig. 1a). Lenticular bodies of chromitite up to 4-8 m in length and with a thickness of about 2 m occur in dunite and are exposed mostly in the southern, less eroded part of the massif. Investigation of accessory PGM in chromitites revealed the dominance of Pt-Fe alloys with subordinate amounts of osmium (Os), laurite (RuS<sub>2</sub>), erlichmanite (OsS<sub>2</sub>), hollingworthite (RhAsS), irarsite (IrAsS), platarsite

(PtAsS), sperrylite (PtAs<sub>2</sub>), tulameenite (Pt<sub>2</sub>CuFe), hongshiite (PtCu), geversite (PtSb<sub>2</sub>), and a number of unnamed phases (Rudashevsky *et al.* 1992a, b, 1994, 1995). This PGM assemblage from chromitites is also consistently found in the Quaternary sediments forming placer deposits closely associated with the Kondyor massif (Rudashevsky *et al.* 1992a, Mochalov & Khoroshilova 1998, Malitch 1999). The new results on osmium-isotope compositions presented in this study are based on PGM separated from chromitite (grains K13, K14, see Fig. 1a for locations), as well as from Quaternary sediments of the Kondyor River in the center of the Kondyor massif (L–204, nuggets K15, K16, K17). Nugget K8 was obtained by panning at the same locality.

The core-zone dunite and associated chromitite lenses are rimmed by metadunite (Fo<sub>78–88</sub>), wehrlite, clinopyroxenite and melanocratic gabbro up to 500 m in thickness (Fig. 1a). The metadunites represent a gradual transitional lithology between dunite and wehrlite. There is also a transition from clinopyroxenites to melanocratic gabbros *via* plagioclase clinopyroxenites.

The core–zone dunites were also intruded by veinlike, fine- to very coarse-grained clinopyroxenites enriched in apatite, biotite and magnetite, forming a stockwork-like zone exposed in the southwestern part of the dunite core (Fig. 1a). The stockwork clinopyroxenites contain cooperite and sperrylite as predominant PGM, plus subordinate Pt–Fe alloys, together with osmium, tulameenite, sobolevskite, braggite, keithconnite, irarsite, malanite, mertieite II, and a number of unnamed Pd-rich phases (Rudashevsky *et al.* 1994). Grain K11 is considered representative of this type of occurrence of Pt–Fe alloy in the stockwork clinopyroxenites.

### The Inagli Massif

The Inagli clinopyroxenite–dunite massif, located in the central part of the Aldan Shield (Fig. 1b), occupies an area of  $32 \text{ km}^2$  and, like Kondyor, exhibits a concentrically zoned structure. This structure is defined by a dunite core and a rim of wehrlite, clinopyroxenite and gabbro (Rozhkov *et al.* 1962, Smirnov 1977, Malitch 1999). In the vicinity of the dunite pipe, a series of alkaline rocks form a laccolithic intrusion. The host rocks of the Inagli massif are the Archean basement of the Siberian Craton and overlying Riphean terrigenous– carbonaceous sequences. As at Kondyor, these rocks form a dome-like structure about 10–12 km in diameter.

The three nuggets (I4, I5, I7) investigated by scanning electron microscopy (SEM), X-ray and electron microprobe (EMP) studies, plus other PGM nuggets (I4, I18, I19) selected for Os-isotope study, were obtained from Quaternary sediments of the Inagli River, which drains the area covered by dunite in the central part of the massif (Fig. 1b).



K - Kondyor, I - Inagli, G - Guli, NT - Nizhny Tagil



FIG. 1. Location and schematic geological maps of the Kondyor (a), Inagli (b) and Guli (c) clinopyroxenite-dunite massifs (modified after Malitch 1999), and the Nizhny Tagil massif (d) (after Barannikov & Volchenko 1997). The location of PGM investigated is indicated.

It is noteworthy that the ultramafic rocks of the Kondyor and Inagli massifs are characterized by a pipelike shape, intruded by alkaline and subalkaline rocks, which at current levels of erosion may constitute 10 to 30%, respectively, of the area of each massif. These alkaline to subalkaline rocks form part of the post-Jurassic Aldan complex (El'yanov & Moralyov 1961, El'vanov & Andreev 1991) and are the reason for contradictory suggestions on the age of the mafic-ultramafic massifs. On the one hand, the Kondyor and Inagli complexes are assumed to be the result of multiple intrusions, from which point of view the ultramafic rocks are considered to be Late Proterozoic, and the alkaline rocks, Mesozoic (El'yanov & Moralyov 1961, Gurovitch et al. 1994). Others suggest that the entire intrusive suites are comagmatic and were formed in the Mesozoic (Orlova 1991, Kogarko et al. 1995). Our Os-isotope results provide new age constraints.

### The Guli Massif

The distinctive feature of the Guli massif, located in the northern part of the Siberian Craton, is its considerable size. According to geological and geophysical data, the massif occupies an area of about 2000 km<sup>2</sup> and is thus the world's largest clinopyroxenite-dunite massif. From 1985 to 1997, geological mapping and exploration campaign on a 1:200000 scale took place, the results of which were recently summarized by Malitch & Lopatin (1997a, b) and Malitch (1999). The Guli massif is controlled by the Taimyr-Baikal and Enisei-Kotui paleorift structures. The exposed part ( $600 \text{ km}^2$ ) of the massif is mainly composed of an ultramafic complex (Fig. 1c), represented by dunite, chromitite, wehrlite and magnetite-bearing clinopyroxenite. Dunite (Fo<sub>85-91</sub>) predominates, forming a crescent-shaped, plate-like body 30 km long and 10-15 km wide covering an area of approximately 450 km<sup>2</sup>, moderately dipping (*i.e.*,  $15-20^{\circ}$ ) to the northwest. To the southwest, the complex is overlain by the Maimechian ultramafic volcanic rocks (known as meimechites), and in the central part, it is penetrated by stock-like bodies of the Maimecha-Kotui ijolite-carbonatite complex (Fig. 1c), which occupies an area of less than 35 km<sup>2</sup> (Egorov 1991, Kogarko et al. 1995, Vasil'ev & Zolotukhin 1995, Fedorenko & Czamanske 1997, and references cited therein). On the basis of recent Os-isotope data, the Guli ultramafic complex was formed in Early Carboniferous time (i.e., model ages of around 370 Ma, Malitch & Kostoyanov 1999), whereas the meimechites and ijolite-carbonatite stocks, dated by Rb-Sr and Nd-Sm methods, were emplaced within the time interval 220-240 Ma (Kogarko et al. 1989, Egorov 1991).

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 had previously been evaluated as promising for apatite, phlogopite, iron, nepheline, rare metals and rare-earth elements (*REE*) associated with the ijolite–carbonatite complexes (*e.g.*, Egorov 1991, Kogarko *et al.* 1995, among others). On the basis of geological, mineralogical and geochemical studies, Malitch & Lopatin (1997a, b) proposed distinct origins for ultramafic and alkaline rock suites within the Guli massif and thus distinguished between the Guli clinopyroxenite–dunite and the Maimecha–Kotui ijolite–carbonatite complexes.

A further peculiarity of the Guli clinopyroxenitedunite complex is that it exhibits transitional features between typical zoned platiniferous clinopyroxenitedunite massifs of the Urals, the Aldan Shield, Russian Far East, Alaska, British Columbia, Eastern Australia (*i.e.*, Alaskan-, Uralian-, and Aldan-type massifs), and typical ophiolitic dunite-harzburgite (*i.e.*, Alpine-type) massifs of the Urals, Koryakia, New Caledonia, Tasmania, Eastern Alps and other regions (e.g., Cabri & Harris 1975, Naldrett & Cabri 1976, Page et al. 1983, Talkington et al. 1984, Barnes et al. 1985, Legendre & Augé 1986, Rudashevsky 1989, Thalhammer et al. 1990, Malitch 1991, 1996a, b, 1998, 1999, Mochalov et al. 1991, Malitch & Rudashevsky 1992, Augé & Legendre 1992, Lazarenkov et al. 1992, Palandzhian et al. 1994, Cabri et al. 1996, Malitch & Lopatin 1997a, b, Foley et al. 1997, Garuti et al. 1997, 1999, Malitch & Augé, 1998, Volchenko & Koroteev 1998, Melcher et al. 1999, Malitch et al. 2001). The assemblage of ultramafic rocks (dunite, chromitite, wehrlite and clinopyroxenite) of the Guli massif and its significant potential for placer formation coincide well with typical zoned massifs of Alaskan-, Uralian- and Aldan-type, whereas the huge size of the ultramafic complex, its shape, the lack of a concentrically zoned structure, and the common occurrence of refractory PGE such as Os and Ir match well with ophiolitic massifs.

The placer deposits of the Guli massif are associated with Upper Quaternary and recent alluvial sediments of the Ingaringda, Sabyda, Gule, and Selingda rivers and their tributaries (Malitch *et al.* 1998). Both fluviatile sediments and terrace beds are productive in PGM and gold. The precious metal nuggets are particularly concentrated in terrace beds and occur preferentially in a sandy-pebbled clayey layer with boulders, especially close to the boundary between unconsolidated sediments and bedrock.

A characteristic feature of the placer deposits of the Guli massif and the other massifs under consideration is the lack of any evidence for a considerable distance of transport of the nuggets from the source, as is clearly indicated by the preservation of crystal shape of the placer minerals (Fig. 2). The gold–PGM placers that developed within the recent drainage-network in the area of the ultramafic bedrock have an alluvial and, probably, partly fluvioglacial origin. Erosion of the ultramafic rocks of the Guli massif began prior to the Cretaceous, because grains of chromite clearly derived from dunite were discovered in terrigenous Early Cretaceous



FIG. 2. Back-scattered electron images showing morphology (a, c, e) and composition (b, d, f) of PGM nuggets G1 (a, b), G2 (c, d) and G6 (e, f) derived from the Guli massif. Pt<sub>3</sub>Fe and Pt<sub>2</sub>Fe: ferroan platinum, LR: laurite, MLN: malanite, MNCH: moncheite, COOP: cooperite, DI: diopside. Numbers 6–11, 16, 23–25 denote areas of electron-microprobe analyses corresponding to the same numbers in Tables 2–4. Scale bar refers to 100 µm.

sediments. Thus, placers were formed during the unroofing and disintegration of ultramafic rocks, followed by subsequent release of precious-metal mineral phases with only short-range mechanical transport by rivers.

The majority of placer PGM associated with the Guli massif have Os–(Ir–Ru)-dominant compositions. Their morphology, physical and chemical properties, textural features, and Os-isotopic composition were summarized by Malitch *et al.* (1995), Malitch & Kostoyanov (1999) and Malitch (1999). A variety of PGM, oxide and silicate inclusions characteristic of such Os–(Ir–Ru) alloys, and unusual polycomponent alloys in the system Ru–Os–Ir–Pt–Fe were first described by Malitch & Augé (1998) and Malitch & Badanina (1998), respectively. A small number of bedrock-hosted PGM also were identified by Malitch & Rudashevsky (1992) and Malitch (1999). However, much less attention has been directed to Pt–Fe alloys prior to the present study.

The Pt–Fe alloy nuggets (G1, G2, G6, G12) investigated in this study were obtained during prospecting in the area of the Gule River (Line 350) in the southern part of the Guli massif (Fig. 1c).

#### The Nizhny Tagil Massif

The Nizhny Tagil massif forms part of the 900-kmlong Platinum Belt of the Urals and represents an undisputable example of the zoned Uralian-type clinopyroxenite-dunite complex (Efimov 1984, 1998). The geology of the Nizhny Tagil massif and associated placers has been presented recently by Barannikov & Volchenko (1997), Genkin (1997) and Volchenko & Koroteev (1998).

The two Pt–Fe alloy nuggets (NT9, NT10) investigated in this study were obtained by panning at the Novy Log placer, located 2.5 km to the east of the Nizhny Tagil massif (Fig. 1d). The Pt–Fe nuggets investigated from Nizhny Tagil are the only ones that were sampled at some distance from the actual source. However, as stressed by Barannikov & Volchenko (1997), the composition of Pt–Fe alloys from the Novy Log placer, represented by isoferroplatinum and tetraferroplatinum, is identical to that of Pt–Fe alloys from the bedrock of the Nizhny Tagil massif (at the type locality, also known as Solov'yova Gora).

### ANALYTICAL TECHNIQUES

Initially, the morphology and size of the nuggets were described under the binocular microscope. More detailed morphological study was carried out using a scanning electron microscope (Camscan–4) at Mekhanobr–Analyt JSC, St. Petersburg, Russia.

Powder-diffraction data for each nugget were obtained using a 57.3-mm-radius Gandolfi camera and an IRIS X-ray generator at the Department of Geology, Moscow State University, Russia. Analytical conditions were 35 kV, 20 mA, unfiltered Cu $K\alpha$ + $\beta$  radiation, with an exposure time of 12 to 28 hours. The data have been corrected for camera diameter and nugget dimensions. The nuggets were positioned in the Gandolfi camera with no prior mechanical treatment (*i.e.*, crushing, grinding, pressing) in order to prevent "secondary" ordering of the structure and to display even weak reflections, where sample diameter exceeded 0.1 mm.

Subsequently, the nuggets were mounted in epoxy resin, carefully ground and polished for optical microscopy and electron-microprobe (EMP) analyses. Mineral compositions were obtained by energy- and wavelengthdispersion (WDS) techniques on an ARL-SEMQ microprobe equipped with a LINK energy-dispersion analyzer at the Institute of Geological Sciences, University of Leoben, Austria. For quantitative WDS analyses, an acceleration potential of 20 or 25 kV, a beam current of 15 or 20 nA, and a beam diameter of approximately 1 µm was used. The following X-ray lines were employed:  $SK\alpha$ ,  $FeK\alpha$ ,  $NiK\alpha$ ,  $CuK\alpha$ ,  $OsM\beta$ ,  $IrL\alpha$ ,  $RuL\alpha$ ,  $RhL\alpha$ ,  $PtL\alpha$  and  $PdL\beta$ . Natural chalcopyrite and pure metals Os, Ir, Ru, Rh, Pt, Pd, Ni were used as standards. Corrections were made for the observed interferences of Ru with Rh, of Ru with Pd, and of Ir with Cu. Analyses of mineral phases less than 3 µm in diameter were considered as semiquantitative because of significant fluorescence from the surrounding host.

Finally, selected PGM grains from the Kondyor and Inagli massifs were removed from the polished resin for the osmium isotopic analysis. The isotopic composition was determined on the individual grains by negative thermal ionization mass-spectrometry (NTI-MS) using a modified MI-1320 instrument (Kostovanov & Pushkaryov 1998, Kostoyanov et al. 2000) at the Department of Isotope Geology, All-Russia Geological Research Institute (VSEGEI), St. Petersburg, Russia. With this method, it is possible to analyze individual PGM grains with a mass of 10<sup>-7</sup> g and an osmium content greater than 10 wt.%. This sample size is sufficient to maintain the signal of the most abundant isotope of Os, <sup>190</sup>Os, within the range of  $10^{-13} - 10^{-14}$  ångström (Å) for several hours. Further details on the method and analytical precisions are given in Malitch et al. (2000). The data obtained were normalized to the <sup>190</sup>Os/<sup>188</sup>Os value of  $1.98379 \pm 0.00002$  according to the "osmium-DTM-standard" measured by NTI-MS on the mass spectrometer MAT-262 (Tuttas 1992).

# CHEMICAL COMPOSITION OF MINERALS

Mineralogical and compositional characteristics have been obtained by microscopic, SEM and EMP studies. Typical morphological features, characteristic textures of Pt–Fe and Os–Ir–Ru–Pt alloys and minute intergrowths of PGM are illustrated in Figures 2 to 5. A list of all the PGM found in the Pt–Fe nuggets is presented in Table 1. Further details on the PGM, oxide and silicate phases included in the Pt–Fe alloys will be presented elsewhere. Os–Ir–Ru–Pt alloys were classified



FIG. 3. Back-scattered electron images of PGM assemblages in Pt–Fe nuggets from the Guli (a, b), Inagli (c, d), Nizhny Tagil (e) and Kondyor (f) clinopyroxenite–dunite massifs. Samples G2 (a), G12 (b), 14 (c), I5 (d), NT10 (e), K11 (f). Pt<sub>3</sub>Fe, Pt<sub>2</sub>Fe and Pt<sub>3</sub>Fe<sub>2</sub>: ferroan platinum, PtFe: tetraferroplatinum (?), Ru: osmian ruthenium, LR: laurite, (Os,Ru,Ir): ruthenian osmium, Ir–Os: osmian iridium, Os: osmium. Numbers 2–4, 7, 12, 14–20, 22 denote areas of electron-microprobe analyses and correspond to those in Tables 2–4. Scale bar refers to 30 μm.



FIG. 4. Composition of nugget I4 from the Inagli placer in back-scattered electron mode and single-element scans for Os, Pt and Ir. Scale bar refers to 35 μm.

according to the nomenclature of Harris & Cabri (1991). Representative results of 118 electronmicroprobe WDS analyses of Pt–Fe alloys are presented in Table 2, those of Os–Ir–Ru–Pt alloys and several other PGM inclusions (from a total of 42 analyses) are shown in Tables 3 and 4 and Figure 6.

### Kondyor

Nugget K8 (about 1.2 mm in diameter) is irregularly shaped and revealed a rather constant composition corresponding to  $Pt_{2.9}Fe_{1.1}$ . The Cu content is in the range of 0.64 to 1.14 wt.%, and no significant amounts of other PGE were detected (Table 2, anal. 1). The nugget hosts



FIG. 5. Composition of nugget G12 from Guli placer in back-scattered electron mode and single-element scans for Os, Ru and Pt. Scale bar refers to 15  $\mu$ m.

some tiny inclusions of laurite, rhodian irarsite, and stibiopalladinite (Table 4, anal. 27).

PGM grain K11 (0.65  $\times$  0.3 mm in size), derived from a clinopyroxenite, seems to be rather homogeneous in composition, and corresponds to the formula (Pt,Pd,Rh)<sub>2.8</sub>(Fe,Cu)<sub>1.2</sub>, with Pd ranging from 7.65 to 8.88 wt.%, Rh 0.62 to 1.24 wt.% and Cu contents below 1.65 wt.% (Table 2, anal. 2). The nugget contains tiny white lamellae (up to 30  $\mu$ m in longest dimension) of nearly pure osmium (Figs. 3f, 6, Table 3, anal. 20).

### Inagli

Nugget I4 is an irregularly rounded two-phase grain (about 0.2 mm in diameter) composed of Pt–Fe and Ir– Os–Pt alloys (Figs. 3c, 4). The composition shows a weakly developed variation with respect to Pt and Rh, and high Ir contents. Ir ranges from 3.95 to 4.28 wt.%, Rh, from 0.87 to 1.45 wt.%, Pt, from 83.60 to 85.36 wt.%, respectively, and Cu does not exceed 0.37 wt.%. The corresponding formula can be presented as (Pt, Ir,

	Nizhny	, Tagil	Kon	dyor	I	nagli					
Mineral	NT9	NT10	K8	K11	14	15	17	G1	G2	G6	G12
Ferroan platinum Pt <sub>3</sub> Fe			٠	٠	٠	•	٠	٠		٠	
Ferroan platinum Pt <sub>2</sub> Fe	•								٠		٠
Ferroan platinum Pt <sub>3</sub> Fe <sub>2</sub>		٠									
Tetraferroplatinum PtFe (?)		•									
Pt-Cu alloy										٠	
Osmium (Os, Os-Ir, Os-Ru-Ir)		•		•					•	٠	
Iridium (Ir-Os)					•	•					
Kuthenium (Ku-Os-Ir)											•
$C_{aur} = KuS_2$			•						•	•	•
Osmian laurite (Ru,Os)S <sub>2</sub>										•	
Malanite CuPt <sub>2</sub> S <sub>4</sub>										٠	
Cuproiridsite CuIr <sub>2</sub> S <sub>4</sub>							•	•			
Unnamed (Fe,Cu,Ni)-(Pt,Ir)-S								•			
Cooperite PtS										٠	
Iridian hollingworthite (Rh,Ir)AsS			•								
Rhodian irarsite (Ir,Rh)AsS							•			•	
Moncheite PtTe <sub>2</sub>										•	
Telluropalladinite Pd9Te4								•			
Stibiopalladinite Pd <sub>5</sub> Sb <sub>2</sub>			•								

TABLE 1. LIST OF PGM OBSERVED IN Pt-Fe NUGGETS ACCORDING TO X-RAY AND ELECTRON-MICROPROBE DATA

• - major PGM, • - minor PGM

Rh)<sub>2.9</sub>(Fe, Cu)<sub>1.1</sub> (Table 2, anal. 3). The Pt–Fe alloy hosts numerous predominantly irregular patches with approximate formula of  $Ir_{0.56}Os_{0.16}Pt_{0.12}Ru_{0.10}Rh_{0.05}$  $Fe_{0.01}$  (Table 3, anal. 17) and one euhedral inclusion (cubic, 35  $\mu$ m in diameter) of osmian iridium (Figs. 3c, 4, 6).

Nugget I5 is a subhedral two-phase grain ( $0.4 \times 0.15$  mm in size) composed of Pt–Fe and Ir–Os–Pt alloys (Fig. 3d). The main mineral phase is an Ir-rich Pt–Fe alloy, (Pt,Ir)<sub>2.9</sub>(Fe,Cu)<sub>1.1</sub>, with Ir contents ranging from 3.67 to 4.55 wt.%, whereas Cu contents are below 0.99 wt.% (Table 2, anal. 4). This Pt–Fe alloy contains abundant roundish inclusions (one about 60 µm in diameter) and patches (about 3–4 µm in diameter) of osmian iridium (Figs. 3d, 6), with an approximate formula of Ir<sub>0.51</sub>Os<sub>0.24</sub> Pt<sub>0.12</sub>Ru<sub>0.10</sub>Rh<sub>0.02</sub>Fe<sub>0.01</sub> (Table 3, anal. 18).

Fractured nugget I7 consists of three pieces of Irrich Pt–Fe alloy with an approximate formula (Pt, Ir)<sub>2.9</sub>(Fe, Cu)<sub>1.1</sub>. Ir contents vary from 3.25 to 4.59 wt.%, and Cu is in the range of 0.87 to 1.48 wt.% (Table 2, anal. 5). A few inclusions of the PGE thiospinel cuproiridsite were found as well as PGE sulfarsenides belonging to the irarsite–hollingworthite solid-solution series, restricted to the boundaries of the nugget. The outer part of the nugget is free of impurities, and its composition corresponds to pure Pt–Fe alloy with a composition close to Pt<sub>3</sub>Fe.

#### Guli

Nugget G1 (0.5  $\times$  0.5 mm in diameter) is cubic in form and hosts a tetragonal polyphase inclusion (45  $\times$ 

35 μm) (Figs. 2a, b). The matrix is (Pt, Pd, Ir)<sub>2.8</sub>Fe<sub>1.2</sub>, with constant chemical composition (Table 2, anal. 6). Pd contents vary from 2.68 to 3.58 wt.%, Ir contents lie in the range of 1.11 to 1.41 wt.%, and the Cu content is below 0.40 wt.%. The polyphase inclusion consists of telluropalladinite, Pd<sub>9</sub>Te<sub>4</sub>, a PGE thiospinel of the cuproiridsite – malanite – cuprorhodsite solid-solution series Cu(Ir,Pt,Rh)<sub>2</sub>S<sub>4</sub> (Fig. 2b, Table 4, anal. 24, 25, respectively), an unnamed base metal – PGE mono-sulfide (Fe, Cu, Ni)(Ir, Pt)S, and chalcopyrite.

The rounded (about 0.6 mm in diameter) polyphase nugget G2 (Figs. 2c, d, 3a) is dominated by Pt–Fe alloy corresponding to a formula (Pt,Rh,Pd,Ir)<sub>2</sub>(Fe,Ni), with no significant compositional variation; Pt ranges from 69.32 to 72.29 wt.%, Ir, from 3.60 to 4.35 wt.%, Pd, from 4.45 to 5.35 wt.%, and Rh, from 5.12 to 6.22 wt.% (Table 2, anal. 7). Cu does not exceed 0.36 wt.%. This Pt–Fe alloy phase is characterized by abundant, oriented lamellae of  $Os_{0.45}Ru_{0.25}Ir_{0.24}Rh_{0.03}Pt_{0.03}$  (Figs. 2d, 3a, 6, Table 3, anal. 16). Laurite (RuS<sub>2</sub>), with 1.6–1.87 wt.% Os and 0.70–0.79 wt.% Ir (Table 4, anal. 23), forms about 20 vol.% of the nugget (Figs. 2c, d).

Nugget G6 (0.6–0.35 mm in diameter, Figs. 2e, f) is irregularly shaped and polyphase, containing a number of PGM listed in Table 1. About half the nugget margin is rounded and half is irregular (Fig. 2f). A Pt–Fe(Cu) alloy, with a strongly variable Fe:Cu ratio (from Pt<sub>3</sub>Fe to Pt<sub>3</sub>Cu) composes the main part of this nugget (Fig. 2f, Table 2, anal. 8–11). The Pt–(Fe,Cu) alloy occasionally hosts white lamellae (less than 1  $\mu$ m in thickness) which, according to semiquantitative analyses, consist of iridian osmium. Furthermore, particularly in the ir-

TABLE 2. REPRESENTATIVE COMPOSITIONS OF Pt-Fe ALLOYS FROM CLINOPYROXENITE-DUNITE COMPLEXES, RUSSIA

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$																
Sample         K8         K11         14         15         17         G1         G2         G6         G6         G6         G1         22         22         22         22         22         0.24         0.79         0.00         0.01         0.01         0.01         0.01 <th>No.</th> <th>1</th> <th>2</th> <th>3</th> <th>4</th> <th>5</th> <th>6</th> <th>7</th> <th>8</th> <th>9</th> <th>10</th> <th>11</th> <th>12</th> <th>13</th> <th>14</th> <th>15</th>	No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Sample	K8	K11	I4	15	I7	G1	G2	G6	G6	G6	G6	G12	NT9	NT10	NT10
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Figure		3f	3c	3d		2b	2d, 3a	2f	2f	2f	2f	3b		3e	3e
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	wt. %															-
Ni         0.11         0.10         0.12         0.22         0.24         0.79         0.00         0.00         0.00         0.53         0.38         0.19           Cu         0.64         1.65         0.22         0.89         1.37         0.40         0.28         9.53         2.36         4.71         3.60         0.38         0.88         0.64           Ru         0.00         0.19         0.13         0.00         0.01         0.20         0.00         0.00         0.00         0.99         0.15         0.00           Rh         0.76         1.24         1.08         1.40         0.93         0.32         5.76         0.66         0.59         0.76         0.71         2.53         0.94         1.06           Pd         0.41         8.88         0.00         0.00         2.93         4.45         0.00         0.00         0.21         0.30         0.00         0.36         0.45           Os         0.00         0.34         0.00         0.25         0.23         0.14         0.23         0.18         0.27         0.23         0.15         0.32         0.20         0.18           Ir         0.41         0.00	Fe	9.83	10.24	9.94	9.51	8.80	10.78	12.79	1.01	7.35	4.64	5.67	12.56	12.09	14.34	17.57
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni	0.11	0.10	0.12	0.22	0.24	0.24	0.79	0.00	0.00	0.00	0.00	0.53	0.38	0.19	0.38
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu	0.64	1.65	0.22	0.89	1.37	0.40	0.28	9.53	2.36	4.71	3.60	0.38	0.88	0.64	1.95
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru	0.00	0.19	0.13	0.00	0.00	0.13	0.20	0.00	0.00	0.00	0.00	0.99	0.15	0.00	0.00
Pd         0.41         8.88         0.00         0.00         2.93         4.45         0.00         0.00         0.21         0.30         0.00         0.36         0.45           Os         0.00         0.34         0.00         0.25         0.23         0.14         0.23         0.18         0.27         0.23         0.15         0.32         0.20         0.18           Ir         0.41         0.00         3.95         3.70         4.30         1.40         3.99         0.17         0.52         0.64         0.00         0.47         2.84         0.47           Pt         88.71         77.59         85.31         84.60         84.95         84.44         72.29         88.04         90.33         89.26         89.52         83.27         82.70         82.35           Total         100.87         100.22         100.75         100.82         100.78         99.59         101.42         100.45         99.95         101.05         100.54         99.68           at.%         Fe         26.82         25.89         27.25         25.97         24.20         28.55         30.97         2.88         20.52         13.22         16.18         31.88 <td< td=""><td>Rh</td><td>0.76</td><td>1.24</td><td>1.08</td><td>1.40</td><td>0.93</td><td>0.32</td><td>5.76</td><td>0.66</td><td>0.59</td><td>0.76</td><td>0.71</td><td>2.53</td><td>0.94</td><td>1.06</td><td>0.93</td></td<>	Rh	0.76	1.24	1.08	1.40	0.93	0.32	5.76	0.66	0.59	0.76	0.71	2.53	0.94	1.06	0.93
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Pd	0.41	8.88	0.00	0.00	0.00	2.93	4.45	0.00	0.00	0.21	0.30	0.00	0.36	0.45	0.5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Os	0.00	0.34	0.00	0.25	0.23	0.14	0.23	0.18	0.27	0.23	0.15	0.32	0.20	0.18	0.13
Pt         88.71         77.59         85.31         84.60         84.95         84.44         72.29         88.04         90.33         89.26         89.52         83.27         82.70         82.35           Total         100.87         100.22         100.75         100.57         100.82         100.78         100.78         99.59         101.42         100.45         99.95         101.05         100.54         99.68           at. %         Fe         26.82         25.89         27.25         25.97         24.20         28.55         30.97         2.88         20.52         13.22         16.18         31.88         31.35         36.16           Ni         0.29         0.24         0.31         0.57         0.63         0.60         1.82         0.00         0.00         0.00         1.28         0.94         0.46           Cu         1.53         3.67         0.53         2.14         3.30         0.92         0.60         23.89         5.80         11.80         9.03         0.84         2.01         1.41           Ru         0.00         0.27         0.20         0.00         0.00         1.9         0.27         0.00         0.00         1.39	Ir	0.41	0.00	3.95	3.70	4.30	1.40	3.99	0.17	0.52	0.64	0.00	0.47	2.84	0.47	0.84
Total         100.87         100.22         100.75         100.87         100.82         100.78         100.78         99.59         101.42         100.45         99.59         101.05         100.54         99.68           at. %         Fe         26.82         25.89         27.25         25.97         24.20         28.55         30.97         2.88         20.52         13.22         16.18         31.88         31.35         36.16           Ni         0.29         0.24         0.31         0.57         0.63         0.60         1.82         0.00         0.00         0.00         1.28         0.94         0.46           Cu         1.53         3.67         0.53         2.14         3.30         0.92         0.60         23.89         5.80         11.80         9.03         0.84         2.01         1.41           Ru         0.00         0.27         0.20         0.00         0.19         0.27         0.00         0.00         1.39         0.42         1.43         1.02         0.89         1.17         1.10         3.49         1.32         1.45           Pd         0.59         11.79         0.00         0.00         0.00         0.00         0.0	Pt	88.71	77.59	85.31	84.60	84.95	84.44	72.29	88.04	90.33	89.26	89.52	83.27	82.70	82.35	77.88
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Total	100.87	100.22	100.75	100.57	100.82	100.78	100.78	99.59	101.42	100.45	99.95	101.05	100.54	99.68	100.18
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	at. %															
Ni         0.29         0.24         0.31         0.57         0.63         0.60         1.82         0.00         0.00         0.00         1.28         0.94         0.46           Cu         1.53         3.67         0.53         2.14         3.30         0.92         0.60         23.89         5.80         11.80         9.03         0.84         2.01         1.41           Ru         0.00         0.27         0.20         0.00         0.00         0.19         0.27         0.00         0.00         1.39         0.21         0.00           Rh         1.13         1.70         1.61         2.07         1.39         0.46         7.58         1.02         0.89         1.17         1.10         3.49         1.32         1.45           Pd         0.59         11.79         0.00         0.00         4.07         5.66         0.00         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25         0.00         0.00         4.07         5.66         0.00         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25 </td <td>Fe</td> <td>26.82</td> <td>25.89</td> <td>27.25</td> <td>25.97</td> <td>24.20</td> <td>28.55</td> <td>30.97</td> <td>2.88</td> <td>20.52</td> <td>13.22</td> <td>16.18</td> <td>31.88</td> <td>31.35</td> <td>36.16</td> <td>40.87</td>	Fe	26.82	25.89	27.25	25.97	24.20	28.55	30.97	2.88	20.52	13.22	16.18	31.88	31.35	36.16	40.87
Cu         1.53         3.67         0.53         2.14         3.30         0.92         0.60         23.89         5.80         11.80         9.03         0.84         2.01         1.41           Ru         0.00         0.27         0.20         0.00         0.01         0.27         0.00         0.00         0.00         0.00         0.00         0.00         0.00         0.00         0.00         1.39         0.21         0.00           Rh         1.13         1.70         1.61         2.07         1.39         0.46         7.58         1.02         0.89         1.17         1.10         3.49         1.32         1.45           Pd         0.59         11.79         0.00         0.00         4.07         5.66         0.00         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25         0.00         0.00         4.07         5.66         0.00         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25         0.00         0.20         0.11         0.16         0.15         0.22         0.19         0.13         0	Ni	0.29	0.24	0.31	0.57	0.63	0.60	1.82	0.00	0.00	0.00	0.00	1.28	0.94	0.46	0.84
Ru         0.00         0.27         0.20         0.00         0.01         0.27         0.00         0.00         0.00         1.39         0.21         0.00           Rh         1.13         1.70         1.61         2.07         1.39         0.46         7.58         1.02         0.89         1.17         1.10         3.49         1.32         1.45           Pd         0.59         11.79         0.00         0.00         4.07         5.66         0.00         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25         0.00         0.20         0.19         0.11         0.16         0.15         0.22         0.19         0.13         0.24         0.15         0.13	Cu	1.53	3.67	0.53	2.14	3.30	0.92	0.60	23.89	5.80	11.80	9.03	0.84	2.01	1.41	3.99
Rh         1.13         1.70         1.61         2.07         1.39         0.46         7.58         1.02         0.89         1.17         1.10         3.49         1.32         1.45           Pd         0.59         11.79         0.00         0.00         4.07         5.66         0.00         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25         0.00         0.20         0.19         0.11         0.16         0.15         0.22         0.19         0.13         0.24         0.15         0.13	Ru	0.00	0.27	0.20	0.00	0.00	0.19	0.27	0.00	0.00	0.00	0.00	1.39	0.21	0.00	0.00
Pd         0.59         11.79         0.00         0.00         4.07         5.66         0.00         0.31         0.45         0.00         0.49         0.60           Os         0.00         0.25         0.00         0.20         0.19         0.11         0.16         0.15         0.22         0.19         0.13         0.24         0.15         0.13	Rh	1.13	1.70	1.61	2.07	1.39	0.46	7.58	1.02	0.89	1.17	1.10	3.49	1.32	1.45	1.17
Os 0.00 0.25 0.00 0.20 0.19 0.11 0.16 0.15 0.22 0.19 0.13 0.24 0.15 0.13	Pd	0.59	11.79	0.00	0.00	0.00	4.07	5.66	0.00	0.00	0.31	0.45	0.00	0.49	0.60	0.61
	Os	0.00	0.25	0.00	0.20	0.19	0.11	0.16	0.15	0.22	0.19	0.13	0.24	0.15	0.13	0.09
Ir 0.33 0.00 3.15 2.93 3.44 1.08 2.81 0.14 0.42 0.53 0.00 0.35 2.14 0.34	Ir	0.33	0.00	3.15	2.93	3.44	1.08	2.81	0.14	0.42	0.53	0.00	0.35	2.14	0.34	0.57
Pt 69.31 56.19 66.95 66.12 66.85 64.02 50.13 71.92 72.15 72.78 73.11 60.53 61.39 59.45	Pt	69.31	56.19	66.95	66.12	66.85	64.02	50.13	71.92	72.15	72.78	73.11	60.53	61.39	59.45	51.86

Numbers 2-4, 6-12, 14 and 15 refer to analysis points on Figs. 2 and 3, respectively. Analyses 1-2 from Kondyor, analyses 3-5 from Inagli, analyses 6-12 from Guli, analyses 13-15 from Nizhny Tagil

#### TABLE 3. REPRESENTATIVE COMPOSITIONS OF Os-Ir-Ru-Pt ALLOYS FROM CLINOPYROXENITE-DUNITE COMPLEXES, RUSSIA

No.	16	17	18	19	20	21
Sample	G2	I4	15	NT10	K11	G12
Figure	2d, 3a	3c	3d	3e	3f	5
Alloy	Os-Ru-Ir	Ir-Os-Pt	Ir-Os-Pt	Os-(Ir-Ru)	Os	Ru-Os-1r
wt. %						
Fe	0.24	0.51	0.47	0.00	0.00	0.00
Ni	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
Ru	15.63	5.77	5.34	3.23	0.00	37.12
Rh	1.83	2.65	1.22	0.47	0.71	0.00
Pd	0.00	0.00	0.00	0.00	0.00	0.00
Os	51.90	16.59	25.09	85.27	98.15	42.36
Ir	27.65	60.70	54.78	9.49	0.00	13.19
Pt	2.93	12.87	12.56	1.02	0.54	8.18
Total	100.18	99.09	99.46	99.48	99.40	100.85
at. %						
Fe	0.71	1.63	1.52	0.00	0.00	0.00
Ni	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
Ru	25.41	10.18	9.53	5.92	0.00	52.43
Rh	2.92	4.59	2.13	0.85	1.31	0.00
Pd	0.00	0.00	0.00	0.00	0.00	0.00
Os	44.84	15.55	23.79	83.11	98.16	31.79
Ir	23.64	56.29	51.42	9.15	0.00	9.80
Pt	2.48	11.76	11.61	0.97	0.53	5.99

Numbers 16-20 refer to analysis points on Figs. 2 and 3, respectively. Analysis 16 = lamella within Pt-Fe alloy of nugget G2 (Guli), analysis 17 = irregular inclusion in nugget 14 (Inagli), analysis 18 = irregular inclusion in nugget 15 (Inagli), analysis 19 = osmium inclusion in nugget NT10 (Nizhny Tagil), analysis 20 = osmium inclusion in nugget K11 (Kondyor), analysis 21 = Ru-rich inclusion in the margin of nugget G12 (Guli) regular part of the nugget, the Pt–Fe alloy contains some darker, irregular spots and patches of cooperite (PtS, Table 4, anal. 26), PGE thiospinel (iridian malanite), moncheite PtTe<sub>2</sub>, and zoned laurite  $RuS_2$  with variable Os contents (Ru,Os)S<sub>2</sub> (Fig. 2f). Some inclusions of PGE sulfarsenides of the irarsite–hollingworthite solid-solution series also were observed.

Nugget G12 is a rounded grain (0.5 mm in size) dominated by (Pt,Rh)<sub>2</sub>Fe (Figs. 3b, 5), with Rh ranging from 1.86 to 2.56 wt.% and Cu contents below 0.49 wt.% (Table 2, anal. 12). An oriented network of slightly darker laths and needles (less than 3  $\mu$ m in thickness) of osmian ruthenium is characteristic (Figs. 3b, 5). Furthermore, at the periphery of the nugget, where thin lamellae essentially of Ru (network) are lacking, small inclusions (up to 20  $\mu$ m in longest dimension) of osmian ruthenium (Figs. 3b, 5, 6, Table 3, anal. 21) occur. The peripheral part of the Pt–Fe nugget also contains some euhedral to subhedral inclusions of laurite (Fig. 3b, Table 4, anal. 22) containing up to 0.56 wt.% Ir and up to 1.15 wt.% Os.

### Nizhny Tagil

Nugget NT9 (about 1.2 mm in size) is an irregularly shaped, homogeneous (Pt,Ir,Rh)<sub>2</sub>(Fe,Cu) alloy, with Ir contents in the range of 2.11 to 2.99 wt.%, Rh from 0.85 to 1.32 wt.%, and Cu contents below 2.01 wt.% (Table 2, anal. 13).

#### TABLE 4. REPRESENTATIVE COMPOSITIONS OF PGE-SULFIDES AND Pd-RICH MINERALS FROM THE GULI AND KONDYOR COMPLEXES

No.	22	23	24	25	26	27
Sample	G12	G2	G1	G1	G6	K8
Figure	3b	2d	2b	2b	2f	
Mineral	Laurite	Laurite	Pd-Te*	TSP*	Cooperite	Pd-Sb*
wt. %						
S	38.01	38.63	0.00	26.25	14.29	0.00
As	n.a.	n.a.	0.00	n.a.	n.a.	1.41
Sb	n.a.	n.a.	0.00	n.a.	n.a.	28.10
Te	n.a.	n.a.	33.07	n.a.	n.a.	n.a.
Bi	n.a.	n.a.	0.00	n.a.	n.a.	0.21
Fe	0.00	0.00	0.00	0.52	0.17	0.14
Ni	0.00	0.00	0.00	0.10	0.00	0.00
Cu	0.00	0.00	0.15	11.25	0.13	0.00
Ru	58.04	58.25	n.a.	0.00	0.00	n.a.
Rh	0.00	0.00	n.a.	8.41	0.47	n.a.
Pd	0.00	0.00	66.32	0.00	0.00	68.51
Os	1.15	1.87	n.a.	0.00	0.33	n.a.
Ir	0.56	0.76	n.a.	27.00	0.30	n.a.
Pt	0.84	0.00	0.20	26.73	84.86	1.06
Total	98.60	99.51	99.74	100.26	100.55	99.43
at. %						
S	66.86	67.12	0.00	59.95	49.88	0.00
As	1		0.00			2.09
Sb			0.00			25.57
Te			29.26			
Bi			0.00			0.11
Fe	0.00	0.00	0.00	0.68	0.34	0.28
Ni	0.00	0.00	0.00	0.12	0.00	0.00
Cu	0.00	0.00	0.26	12.96	0.22	0.00
Ru	32.40	32.11		0.00	0.00	
Rh	0.00	0.00		5.98	0.51	
Pd	0.00	0.00	70.36	0.00	0.00	71.35
Os	0.34	0.55		0.00	0.19	
Ir	0.16	0.22		10.28	0.17	
Pt	0.24	0.00	0.12	10.03	48.69	0.60

Numbers 22-25 refer to analysis points on Figs. 2 and 3, respectively. \* abbreviations of PGM: Pd-Te - telluropalladinite; TSP - Pt-Rh-rich cuproiridsite; Pd-Sb - stibiopalladinite; n.a. element not analyzed. Analysis 22 = laurite inclusion in nugget G12, analysis 23 = laurite inclusion in nugget G2, analysis 24 = telluropalladinite from polyphase inclusion in nugget G1, analysis 25 = Ir-Pt-rich thiospinel from polyphase inclusion in nugget G1, analysis 26 = cooperite inclusion in the margin of nugget G6, analysis 27 = stibiopalladinite inclusion in nugget K8.

Nugget NT10 ( $1.2 \times 1.0 \text{ mm}$  in size) is an irregularly shaped Pt–Fe alloy with unusual chemical composition. The corresponding formula can be presented as Pt<sub>3</sub>(Fe,Cu)<sub>2</sub> to Pt<sub>5</sub>(Fe,Cu)<sub>3</sub> (Table 2, anal. 14), with some lamellae of osmium alloy up to 90 µm long and 10 µm wide (Figs. 3e, 6, Table 3, anal. 19). SEM images show that the Pt–Fe alloy matrix contains darker, thin and oriented lamellae with a composition close to Pt<sub>1.1</sub>(Fe, Cu)<sub>0.9</sub> (Fig. 3e, Table 2, anal. 15). In comparison with Cu and Fe contents in the matrix (<1.10 wt.% and from 13.86 to 14.54 wt.%, respectively), the lamellae contain 1.68 to 1.95 wt.% Cu and 16.74 to 17.57 wt.% Fe, respectively.

# X-RAY DATA

According to Cabri & Feather (1975), there are four Pt–Fe alloys: 1) *native platinum* with a disordered facecentered cubic (*fcc*) structure (space group *Fm3m*)



FIG. 6. Composition of Os–Ir–Ru–Pt alloy inclusions in Pt–Fe alloys in the Os–Ir–Ru and Ir–Os–Pt diagram. The compositional field (dashed lines) for solitary Os–Ir nuggets from the Guli massif (Malitch *et al.* 1995, Malitch & Lopatin 1997b) is shown for comparison. The nomenclature and miscibility gap (shaded) are those of Harris & Cabri (1991).

and >80 at.% Pt, 2) *ferroan platinum* with a disordered *fcc* structure and a Fe content between 20 and 50 at.%, 3) *isoferroplatinum* showing an ordered primitive cubic (*pc*) structure (space group *Pm3m*) and Fe contents most likely ranging between 25 and 35 at.%, and 4) *tetraferroplatinum* with tetragonal symmetry (space group *P4/mmm*) and Fe contents probably between 45 and 55 at.%, or close to PtFe. All these structures are rather similarly displayed in X-ray powder diffractograms, particularly the *fcc* and *pc* symmetries, which makes a clear distinction between *isoferroplatinum* and *ferroan platinum* difficult (Cabri & Feather 1975, Cabri *et al.* 1996).

X-ray data for 11 Pt–Fe nuggets investigated are summarized in Table 5. A clear distinction of the Pt–Fe species is difficult owing to the generally poor diffraction properties of the alloys. The reflection intensity of

TABLE 5. X-RAY DATA OF Pt-Fe ALLOYS FROM CLINOPYROXENITE-DUNITE COMPLEXES, RUSSIA

Sample		G1		G2		G6	(	G12		I4		15		17		K8	ł	K11	N	JT9	N	T10
hkl	Ι	d Å	Ι	d Å	Ι	d Å	I	d Å	Ι	d Å	I	d Å	Ι	d Å	I	d Å	I	d Å	I	dÅ	I	dÅ
111	9	2.22	10	2.185	3	2.227	10	2.227	10	2.23	10	2.22	10	2.227	10	2.227	10	2.232	10	2.227	10	2.227
002	10	1.918	9	1.903	10	1.910	10	1.933	10	1.941	10	1.926	10	1.918	8	1.926	8	1.933	4	1.933	4	1.941
022	6	1.358	10	1.351	3	1.366	8	1.363	10	1.366	10	1.364	8b	1.359	8	1.364	10	1.373	10	1.360	6	1.352
113	10	1.161	10b	1.151	1	1.168	10	1.159	5	1.170	10	1.169	8b	1.158	10	1.163	10	1.163	6	1.159	10b	1.161
222	3	1.113	4	1.104	3	1.132	1	1.116	2	1.120	2	1.120	8b	1.104	2	1.115	1	1.113	4b	1.114	3b	1.112
133	6b	0.886	2b	0.888	2b	0.890	6	0.885	10	0.888	10b	0.888	6b	0.885	10b	0.883	10	0.883	10	0.884	6	0.881
a <sub>av</sub> Å	3.	8484	3.	8193	3.	8663	3.	8584	3.	8701	3.	8623	3.	8440	3.	8582	3.	8650	3.	8558	3.	8547
∆a Å	0.	0096	0.	0255	0.	0321	0.	0083	0.	0208	0.	0137	0.	0139	0.	0038	0.	0100	0.	0087	0.0	0087

G1, G2, G6 and G12 from Guli, 14, 15 and 17 from Inagli, K8 and K11 from Kondyor, NT9 and NT10 from Nizhny Tagil

some powder diagrams is relatively low because of high absorption. A specific feature of the diffraction patterns obtained from some of the nuggets is a broadening of particular peaks. "Broad" reflections, particularly with d around 2.20 Å, are characteristic of nuggets G2, NT9 and NT10. This feature may correspond to the presence of two Pt–Fe phases, probably cubic and tetragonal. However, a definite distinction is impossible because the characteristic peaks are not sufficiently pronounced.

Apart of the main reflections of Pt–Fe alloy at (111), (200), (220), (222) and (331), several additional reflections are obtained in most samples. These could be identified as peaks of Os–Ir–Ru, Ru–Os–Ir alloys, laurite and other associated minerals, in accordance with observations by microscopy and electron-microprobe results. No reflections characteristic of the ordered primitive cubic structure of *isoferroplatinum (Pm3m)* [*i.e.*, (100), (110), (210), (211)], or *tetraferroplatinum (P4/mmm)* [*i.e.*, (200) – (002), (311) – (113)] could be identified. Therefore, all the investigated Pt–Fe alloys reveal a disordered face-centered cubic (*fcc*) structure diagnostic of *ferroan platinum* according to the nomenclature of Cabri & Feather (1975).

The values of the cell parameter  $a_0$  (Table 5) calculated on the basis of a *fcc* structure are generally in agreement with values for cubic Pt–Fe compounds (Cabri & Feather 1975, Cabri & Laflamme 1997). However, there are some significant deviations, particularly from values of pure synthetic Pt–Fe species, owing to minor amounts of Os, Ir, Rh, Pd, Cu and Ni, as will be discussed later.

# **OSMIUM-ISOTOPE DATA**

The <sup>187</sup>Os/<sup>188</sup>Os values of Os–Ir alloys included in Pt–Fe grains from chromitites and associated placers of the Kondyor massif and from placer nuggets of the Inagli massif are listed in Table 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 <sup>187</sup>Re is negligible. Hence, the value of <sup>187</sup>Os/ <sup>188</sup>Os in the PGM under discussion corresponds to that in the source of the ore material at the time of PGM formation. The <sup>187</sup>Os/<sup>188</sup>Os ratios in the PGM from both massifs vary between 0.1248 and 0.1252 (Table 6). The average Os-isotope ratio for PGM (e.g., osmium, iridian osmium, osmian iridium) differs insignificantly with respect to the two massifs, as well as within both localities (i.e.,  $0.1250 \pm 0.002$  for Kondyor and  $0.1249 \pm$ 0.001 for Inagli, respectively; the errors correspond to the 95% confidence interval: Table 6). Therefore, isotopic fractionation among the various Os-rich minerals is insignificant. The measured Os-isotope compositions for PGM correspond to those suggested for the mantle and mantle peridotites. The mantle has a relatively low <sup>187</sup>Os/<sup>188</sup>Os value as a result of evolution in a low Re/

TABLE 6. 11708/11408 VALUES AND MODEL 08-ISOTOPE AGES OF PGM FROM THE KONDYOR AND INAGLI CLINOPYROXENITE – DUNITE MASSIFS

Massif, sample, mineral	Atomic proportions	<sup>187</sup> Os/ <sup>188</sup> Os**	Ma***	
Kondvor				
K13, osmium*	$Os_{0.94}Ir_{0.03}Ru_{0.01}$	0.1248	373	
K14, osmium*	Oso estra Run al Ptan	0.1252	315	
K15, osmium	OsamIra RuamPtam	0.1252	315	
K16, osmium	OsoscIrouRuomPton	0.1248	373	
K17, iridian osmium	Os <sub>0.73</sub> Ir <sub>0.19</sub> Ru <sub>0.07</sub> Pt <sub>0.01</sub>	0.1252	315	
Inagli				
I4, osmian iridium	Iras Osa sePta 12Rua 11Rhaas	0.1250	344	
I6, osmium	Osaslra 2Rua Ptan	0.1249	358	
I7, osmium	Os <sub>0.80</sub> Ir <sub>0.12</sub> Ru <sub>0.05</sub> Pt <sub>0.03</sub>	0.1249	358	

PGM samples are from: (1) the chromitites (\*) and (2)placers. The analyzed Os-rich mineral grains are inclusions or lamellae in ferroan platinum. \*\* Normalized to 190<sub>Os</sub>/188<sub>Os</sub> = 1.98379 (Tuttas 1992). \*\*\* Model ages were calculated according to equation (1), in which the estimate of the present-day undifferentiated mantle reservoir (18<sup>7</sup>Os<sup>1180</sup>Os = 0.12736) is after Yin *et al.* (1996).

Os environment (Hattori & Hart 1991, Luck & Allègre 1991, Walker *et al.* 1996).

Since the <sup>187</sup>Os/<sup>188</sup>Os values in all analyzed PGM do not exceed the value of the contemporary undifferentiated mantle material (CHUR)  $(0.12736 \pm 0.00016)$ (Yin et al. 1996), a model Re-Os age can be calculated according to the method of Allègre & Luck (1980). The Re/Os value of the Earth as a whole (*i.e.*, Bulk Earth) and, in particular for the mantle, has not changed during the 4.5 Ga of geological history, which allows the assumption that model Re/Os ages for rocks of mantle origin are close to real ones. This is particularly true for Os-rich mantle minerals, because their ages cannot be underestimated. Overestimation of ages is also unlikely, since the Re-Os isotope system at the mineral level is relatively resistant to crustal contamination, as has been demonstrated for detrital 3.1 Ga Os-rich alloys from the Evander goldfield, eastern Witwatersrand, South Africa (Malitch et al. 2000). For the calculation of model (mantle-derived) ages, the contemporary and primary <sup>187</sup>Os/<sup>188</sup>Os values in the undifferentiated mantle reservoir are considered to be  $0.12736 \pm 0.00016$  and  $0.09600 \pm 0.00035$ , respectively (Yin *et al.* 1996). Thus, the model Os-isotope age is given by  $(0.12736 - {}^{187}\text{Os}/$ <sup>188</sup>Os) / 0.006862 (Ga), where <sup>187</sup>Os/<sup>188</sup>Os in this expression is the value measured in the sample.

According to the above formula, the mean value of the Os-isotope ratio of PGM from the Kondyor and Inagli massifs yields model <sup>187</sup>Os/<sup>188</sup>Os ages of around 340 and 355 Ma, respectively.

#### DISCUSSION

#### Nomenclature of Pt-Fe alloys

The X-ray powder data indicate that the majority of the grains of Pt-Fe alloys from nuggets derived from clinopyroxenite dunite massifs of the Siberian Craton are ferroan platinum (i.e., K8, K11 from Kondyor, I4. I5, I7 from Inagli, and G1, G6 from Guli) with a disordered face-centered cubic cell (space group Fm3m), although the alloys reveal a composition close to Pt<sub>3</sub>Fe. This result agrees well with the finding of Cabri et al. (1996), that many Pt-Fe alloys close to Pt<sub>3</sub>Fe are erroneously called isoferroplatinum. However, there seems to be an additional complexity with respect to the presence of isoferroplatinum or ferroan platinum: the dominance of one or the other Pt-Fe alloy phase seems to depend also on the host rock, *i.e.*, chromitite, dunite, or clinopyroxenite. A typical example of this complexity can be shown by Pt-Fe allovs from placers associated with the Kondyor massif. Grains of Pt-Fe alloy derived from chromitite hosted in dunite were identified as Irrich isoferroplatinum by Mochalov et al. (1988) and Rudashevsky (1989), whereas Pd-rich alloys derived from clinopyroxenites are *ferroan platinum*, as shown in this study.

Pt-Fe alloys G2, G12 (Guli), and NT9 (Nizhny Tagil) have a composition close to Pt<sub>2</sub>Fe (Table 2, anal. 7, 12, 13), whereas nugget NT10 (Nizhny Tagil) has a composition close to Pt<sub>3</sub>Fe<sub>2</sub> (Table 2, anal. 14). Phases with compositions such as Pt<sub>2</sub>Fe and Pt<sub>3</sub>Fe<sub>2</sub> are not known in the synthetic system Pt-Fe (Kubachewski 1982, Massalski 1986), although there are many naturally occurring Pt-Fe alloys with a composition close to Pt2Fe (Cabri et al. 1996, Distler et al. 1996, Weiser & Bachmann 1999, Sluzhenikin 2000). Zhernovsky et al. (1985) suggested the existence of a "phase heterogeneity" due to the presence of two distinct and intergrown Pt-Fe alloy phases. According to their X-ray investigations, Pt<sub>2</sub>Fe is the result of an intimate intergrowth of Pt<sub>3</sub>Fe and PtFe at a scale of less than 1 µm. In our study, a "heterogeneity" is detected in nugget NT10 from Nizhny Tagil (Fig. 3e, Table 2, anal. 14, 15), where a matrix of Pt<sub>3</sub>Fe<sub>2</sub> and a network of thin (< 3 µm) oriented lamellae of composition close to PtFe are clearly distinguished, and the presence of two Pt-Fe alloy phases is also indicated by our X-ray study (i.e., "broad" reflections). However, Pt-Fe alloys from nuggets G12 (Guli) and NT9 (Nizhny Tagil) are different. Grain NT9 shows a homogeneous composition close to Pt<sub>2</sub>Fe (Table 2, anal. 13) without any sign of a second intergrown Pt-Fe alloy phase, even under high magnification (>20000 times). Nugget G12 exhibits a fine network of osmian ruthenium (Figs. 3b, 5), but no second Pt-Fe alloy phase was detected under the SEM. Therefore, the question whether there are more than two Pt-Fe alloy phases (i.e., native platinum and ferroan platinum, according to Cabri & Feather 1975) existing with a disordered fcc cell structure in the system Pt-Fe remains open. On the basis of the present study, we suggest the addition of two more Pt-Fe alloy phases in the system Pt-Fe, although further investigations with Xray and high-resolution transmission electron microscopy are required.

In Figure 7, the cell edges a of the Pt–Fe alloys are plotted against their compositions with respect to  $\Sigma PGE$ in the Pt-site and Fe + Cu + Ni, respectively. In most samples, the unit-cell edges deviate quite significantly from the regression line derived from synthetic samples of the face-centered cubic alloy (Cabri & Feather 1975). On the other hand, rather good agreement is shown for alloys K8 (Kondyor), I5 (Inagli), and G1, G6 (Guli) (Fig. 7). We assume that the deviations of the unit-cell edges from pure synthetic alloys are the result of impurities, particularly at the Pt site. Ir contents up to 3.70 at.% (e.g., sample I7, Inagli), Pd contents of up to 11.79 at.% (e.g., K11, Kondvor), and Rh contents up to 8.10 at.% (e.g., G2, Guli) were detected, whereas Pt-Fe alloys with minimal impurities match better with the synthetic Pt-Fe phase (Fig. 7a). In general, there is a trend to an increase in the unit-cell edge with increase in other PGE substituting for Pt (Fig. 7a). The clear mismatch of alloys from nuggets NT10 and NT9 (Nizhny Tagil)



FIG. 7. Cell edge *versus* atom per cent Pt + (Os,Ir,Ru,Rh,Pd)
(a) and Fe + (Cu,Ni) (b) for Pt–Fe alloys. Regression lines for *fcc* and *pc* cell after Cabri & Feather (1975).

may be explained by their compositional characteristics, *i.e.*, Pt<sub>3</sub>Fe<sub>2</sub>–PtFe and Pt<sub>2</sub>Fe, respectively, and supports the suggestion that these alloys might represent additional species in the system Pt–Fe.

### The source of the Pt-Fe nuggets

The derivation of the Pt–Fe nuggets investigated from the respective clinopyroxenite–dunite massif is obvious, because the placer deposits display a close spatial association with the massifs. Furthermore, primary PGM from the host rocks were studied previously from Kondyor, Guli and Nizhny Tagil, and these share mineralogical and compositional characteristics with the placer PGM (Cabri & Genkin, 1991, Malitch & Rudashevsky 1992, Rudashevsky *et al.* 1992a, b, 1994, 1995, Cabri *et al.* 1996, Okrugin 1998, Mochalov &

Khoroshilova 1998, Malitch 1999). Our data provide further indications of the host rock of a particular nugget. Ferroan platinum from grain K11 (Kondyor) that was derived directly from a clinopyroxenite host is characterized by high content of Pd (Table 2, anal. 2). Similar results were obtained by Rudashevsky et al. (1994) from the Kondyor massif. High Pd contents were also documented in Pt-Fe alloys from a clinopyroxenite host-rock of the Owendale zoned complex (Johan et al. 1989), as well as in Pt-Fe nuggets from alluvial placers in Madagascar having a proposed Alaskan-type source (Augé & Legendre 1992). On the other hand, ferroan platinum from nuggets I4, I5 and I7 (Inagli) contains high contents of Ir (Table 2, anal. 3-5), which is generally accepted as a characteristic feature of PGM derived from chromitite of zoned ultramafic massifs (Rudazevsky et al. 1992a, b, 1994). Therefore, it seems very likely that nuggets I4, I5 and I7 were derived from chromitite hosted in the dunite core of the Inagli massif.

The set of PGM observed as inclusions in the Pt-Fe alloys, as well as the compositional characteristics of the latter, are generally consistent with previous reports on these four massifs (e.g., Razin 1976, Cabri & Genkin 1991, Rudashevsky et al. 1992a, b, Mochalov et al. 1991, Borg & Hattori 1997, Tolstykh & Krivenko 1997, Malitch & Lopatin 1997b, Okrugin 1998, Malitch 1999). However, our data show that Pt-Fe alloys from Nizhny Tagil are more Fe-rich and poorer in other PGE substituting for Pt than those from the typical zoned Aldan-type massifs of Kondyor and Inagli. Osmium inclusions in Pt-Fe alloys from Nizhny Tagil are similar to those from Aldan-type massifs, ranging from pure osmium to osmian iridium. They are typical of zoned ultramafic massifs (Toma & Murphy 1977, Rudashevsky 1989, Cabri & Genkin 1991, Cabri et al. 1996, Malitch 1999, and this study, Figs. 3c-f, 4, 6). In the Guli massif, solitary osmium minerals, which represent by far the most abundant PGM, are compositionally compatible with Os-Ir and Ir-Os inclusions in Pt-Fe alloys from zoned ultramafic complexes (Cabri et al. 1981, Nixon et al. 1990, Johan et al. 1991, Slansky et al. 1991, Evstigneeva et al. 1992, Malitch et al. 1995, Cabri et al. 1996, Malitch & Lopatin 1997b, and this study, Fig. 6). Inclusions in Pt-Fe alloys from Guli, however, are invariably enriched in Ru, ranging from Ru-rich iridian osmium (G2, Figs. 2d, 3a, 6) to osmian ruthenium (G12, Figs. 3b, 5, 6). Such compositional characteristics are more common for PGM from ophiolite-type sources (Bird & Bassett 1980, Legendre & Augé 1986, Rudashevsky 1989, Mochalov et al. 1991, Palandzhian et al. 1994, Cabri et al. 1996, Krstić & Tarkian 1997, Nakagawa & Franco 1997), and is the reason why the Guli massif is considered to occupy a position intermediate between typical zoned-type and ophiolite-type complexes, as mentioned earlier. On the other hand, the presence of moncheite, PGE-rich thiospinels of the malanite - cuproiridsite - cuprorhodsite solid-solution series in ferroan platinum at Guli

are a characteristic feature of zoned ultramafic massifs. These results give further indication of the type of massif that is the source of the PGE nuggets and point to a useful tool for provenance studies, in cases where the source rocks of placer deposits are uncertain or even unknown (Hagen *et al.* 1990, Johan *et al.* 1990, 2000, Augé & Legendre 1992, Gornostayev *et al.* 1999, Weiser & Bachmann 1999).

### Formation of PGM and Os-isotope constraints

Pt-Fe, Os-Ir-Ru alloys and traces of laurite form at a very early stage of magmatic differentiation under low fugacity of sulfur, high-temperature conditions and, most likely, the presence of a fluid phase, according to experimental results and natural observations (e.g., Johan et al. 1989, Amossé et al. 1992, 2000). All the Pt-Fe alloys investigated reveal a disordered fcc structure, indicating the formation under even higher temperatures than those with ordered structures, as proposed by Johan et al. (1989). As magmatic differentiation continues [e.g., with increasing  $f(O_2)$  and  $f(S_2)$ ], Os-Ir phases exsolve from Pt-Fe alloys. This is suggested by the common occurrence of oriented lamellae of Os-Ir phases in Pt-Fe alloys (Fig. 3), and is interpreted in light of the large miscibility-gaps in the binary systems Os-Ir, Ir-Pt and Os-Pt, respectively (Vacher et al. 1954,

Raub & Plate 1956, Hansen & Anderko 1958, Raub 1964. Voronova et al. 1984). Examination of equilibrium conditions among Pt-Fe, Os-Ir and Ir-Os alloys is illustrated in Figure 8, which is a projection of the two-phase assemblages onto the pseudoternary system Pt+(Fe) – Os+(Ru) – Ir+(Rh) (Vacher et al. 1954, Raub & Plate 1956, Raub 1964, Slansky et al. 1991). Estimated equilibrium temperatures for the Pt-Fe, Os-Ir and Ir-Os alloys are in the range of 850 to 800°C (Fig. 8). These temperature estimates agree well with studies of PGM associations from Fifield (New South Wales, Australia; Slansky et al. 1991), Inagli massif (Tolstykh & Krivenko 1997), and from the Kompiam area (Papua New Guinea; Johan et al. 2000). The final stages of magmatic differentiation are indicated by formation of cooperite (PtS), PGE sulfarsenides and Pt-Pd tellurides and antimonides, occurring as inclusions close to the rim of nuggets from Kondyor, Inagli and Guli.

The dominant role of Pt–Fe alloys in zoned ultramafic massifs is a very pronounced feature, particularly if compared with ophiolite-type massifs and stratiform complexes. This feature is well expressed by "M"shaped chondrite-normalized PGE patterns (Fominykh & Khvostova 1970, Avdontsev & Malitch 1989, Malitch 1990, 1998, Nixon *et al.* 1990, Lazarenkov *et al.* 1992, Zientek *et al.* 1992). Two maxima in the PGE distribution patterns (*i.e.*, at Ir and at Pt, respectively) charac-



FIG. 8. Pseudoternary phase diagram of the Pt(+Fe) – Os(+Ru) – Ir(+Rh) system illustrating the temperature estimates for Os and Ir alloys exsolved from Pt–Fe alloys. Points A and B indicate miscibility limits from experimental data (Vacher *et al.* 1954, Raub 1964). Isotherms are estimated from the binary solvus in the system Pt–Ir (Raub & Plate 1956).

terize chromitites and PGM mineral concentrates from zoned ultramafic massifs, clearly distinct from those of podiform and stratiform chromitites in ophiolites and layered complexes (Page *et al.* 1983, Barnes *et al.* 1985, Naldrett & Von Gruenewaldt 1989, Leblanc 1991, Yang *et al.* 1995, Augé *et al.* 1998, Melcher *et al.* 1999, Malitch *et al.* 2001). This finding is consistent with the observations of Fleet & Stone (1991), that PGE fractionate between alloy and sulfide liquid according to their atomic weight rather than melting point. Thus Ru– Rh–Pd will concentrate preferentially in sulfides, and Os–Ir–Pt in alloys.

Early formation of Pt-Fe alloys with Os-Ir-Ru inclusions at high temperatures implies that the Os-isotopic composition of Os-Ir-Ru alloys should reflect the source region. Therefore, the low <sup>187</sup>Os/<sup>188</sup>Os values obtained, corresponding to Os-isotopic composition of the mantle, and constant Os isotopic ratio within each massif (i.e., Kondyor and Inagli), clearly indicate a common mantle-source for the PGE. The 187Os/188Os values of the PGM nuggets investigated are close to those for the Guli, Nizhny Tagil and certain other zoned clinopyroxenite-dunite complexes (Hattori & Hart 1991, Hattori & Cabri 1992, Borg & Hattori 1997, Malitch & Kostoyanov 1999). The very narrow range of <sup>187</sup>Os/<sup>188</sup>Os values that we found indicates a highly productive single-stage formation of PGM. Most likely, the ore-forming system, invariably related to dunites, was driven by mantle-derived fluids that mobilized and concentrated chromite and PGE to the upper parts of the dunite bodies during their ascent in a semiductile state. This hypothesis could explain the fact that apical parts of the massifs are enriched in chromitites, representing the most important PGE source for platinum placers. Further, we propose that the PGE were derived from the mantle without any significant contribution of crustal Os, and that the <sup>187</sup>Os/<sup>188</sup>Os values have remained unchanged by processes such as transport, sedimentation and weathering during placer formation. This conclusion is consistent with the results of Hattori & Cabri (1992), but conflicts with the assumption that PGE nuggets were formed as secondary phases during river transport (Cousins & Kinloch 1976, Bowles 1986, 1990).

Os-isotope model ages of 340 and 355 Ma for the Kondyor and Inagli massif, respectively, correspond to a late Devonian – early Carboniferous  $(D_3-C_1)$  age of formation for the two massifs. The ultramafic massifs are thus older than the spatially associated alkaline suite (*i.e.*, part of the post-Jurassic Aldan Complex). The ages imply that they are genetically distinct. This Middle Paleozoic time represents a significant stage in the development of the Siberian Craton, characterized by upwelling of the mantle and repeated reactivation of deep, older fractures in the mantle to become rift zones (Malitch 1975, Malitch 1999). Therefore, all clinopyroxenite–dunite massifs of the Siberian Craton are located in zones of long-term deep faults that were formed in the Proterozoic and repeatedly regenerated

during a younger episode of rifting. In a tectonic sense, the clinopyroxenite–dunite massifs of the Siberian Craton, particularly Kondyor and Inagli from the Aldan Province, show close similarities to the Yubdo zoned ultramafic massif, Ethiopia (Duparc & Molly 1928, Augustithis 1965, Cabri *et al.* 1981, Evstigneeva *et al.* 1992). In addition to containing almost identical rocktypes and mineralogy, all these massifs are situated in stable cratons and are not related to mobile orogenic belts.

### CONCLUSIONS

(1) The Pt–Fe alloys investigated with chemical compositions close to  $Pt_3Fe$  are *ferroan platinum* with a disordered *fcc* structure on the basis of X-ray studies. This result clearly shows the necessity of structural determinations, as stressed by Cabri *et al.* (1996), to identify the particular Pt–Fe alloy species; compositional characteristics (*i.e.*, the Pt:Fe ratio) clearly are not diagnostic of the presence of *isoferroplatinum* or *ferroan platinum*.

(2) Three grains of Pt–Fe alloy from Guli (G2, G12) and Nizhny Tagil (NT9), respectively, reveal a composition close to  $Pt_2Fe$  and have a disordered *fcc* structure consistent with *ferroan platinum*. Nugget NT10 from Nizhny Tagil shows intimate intergrowths of two clearly distinguishable Pt–Fe phases, *i.e.*,  $Pt_3Fe_2$  and PtFe. The Pt–Fe system seems to be more complex than our present knowledge provides. On the basis of our present data, we tentatively propose that there may be more than the four known Pt–Fe phases (*cf.* the nomenclature of Cabri & Feather 1975).

(3) Pd-rich *ferroan platinum*, clearly derived from clinopyroxenite host-rocks of the Kondyor massif, and Ir-rich *ferroan platinum* nuggets, most likely coming from chromitites of the Inagli massif, are considered a diagnostic feature of zoned-type ultramafic complexes. Such compositional characteristics give an indication of the source rock of the particular Pt–Fe nugget in cases where the source is unknown.

(4) The compositional characteristics of Ru–Os–Ir inclusions in Pt–Fe alloys from Guli are similar to these PGM phases in ophiolite complexes, whereas the general set of PGM from Guli Pt–Fe nuggets compares well with typical zoned ultramafic massifs such as Kondyor, Inagli and Nizhny Tagil. These results accord with the general geology of the Guli massif, suggested to represent an intermediate position between typical ophiolite complexes and zoned ultramafic massifs.

(5) Low <sup>187</sup>Os/<sup>188</sup>Os values and a very narrow range of these values in Os–Ir minerals investigated from the Kondyor and Inagli massifs clearly indicate a common mantle-source for the PGE. The Os-isotope results further show that the Re–Os system represented by PGM of the intrusive rocks remained unchanged from the time of formation of the PGM until now. There was thus one single event of PGE concentration and PGM formation during the evolution of the typical zoned massifs of Kondyor and Inagli. Os-isotope model ages indicate that this major event took place at the Devonian–Carboniferous boundary, which represented a tectonically very active time in the development of the Siberian Craton.

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