

ORIGIN OF PLATINUM-GROUP-MINERAL NUGGETS INFERRED FROM AN OSMIUM-ISOTOPE STUDY

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ABSTRACT

Osmium-isotope ratios of individual PGM (platinum-group minerals) were determined *in situ* using an ion microprobe. All samples except for one came from placers associated with Alpine- or Alaskan-type ultramafic intrusions. Most Alpine-type samples are Os-Ir-Ru alloys, and most Alaskan-type samples are Pt-Fe alloys (isoferroplatiniun or tetraferroplatiniun), which contain Os-Ir-Ru alloys and laurite/erlichmanite. Osmium-isotope measurements for the Pt-Fe alloys were carried out on those Os-bearing inclusions. The Os-isotope values are similar between cores and rims of PGM and among different inclusions of different phases within individual nuggets. No isotopic variations are observed in PGM that show profound chemical zoning. The lack of isotopic heterogeneity in individual nuggets precludes a low-temperature origin for the nuggets of PGM. $^{187}\text{Os}/^{186}\text{Os}$ values of all samples show a narrow spread, ranging from 0.99 to 1.12, with most of the values between 1.00 and 1.06. These values fall within the range of $^{187}\text{Os}/^{186}\text{Os}$ values of the mantle, suggesting essential derivation of platinum-group elements (PGE) from the mantle without a significant contribution of crustal Os. The grains of PGM were formed in intrusions, weathered, eroded, and concentrated in placers by mechanical processes. The Os-isotopic data are consistent with the occurrence of exsolution lamellae of PGM, the inclusions of pristine unweathered olivine, and the lack of "foreign" mineral inclusions, unrelated to ultramafic rocks, within the nuggets. Os-isotopic values for a placer nugget and PGM from chromitite in Urals also support the conclusion that the placer nugget was derived from the latter. The irregular shape and nonabraded surfaces of some nuggets may simply reflect their durable nature and a short distance of transport from the eroded ultramafic intrusions.

Keywords: osmium isotopes, placer, platinum nuggets, platinum-group minerals, Alaskan-type, Alpine-type, ultramafic intrusions.

SOMMAIRE

Le rapport des isotopes 187 et 186 de l'osmium dans les minéraux du groupe du platine (MGP) a été déterminé *in situ* au moyen d'une microsonde ionique. Tous les échantillons sauf un proviennent de graviers alluvionnaires associés à des massifs ultramafiques alpins ou de type Alaska. La plupart des échantillons de massifs alpins consistent d'alliages de Os-Ir-Ru, tandis que la plupart des échantillons de massifs de type "Alaska" sont des alliages de Pt-Fe (isoferroplatine ou tétraferroplatine), qui contiennent aussi des alliages Os-Ir-Ru et laurite ou erlichmanite. Les mesures isotopiques des échantillons d'alliage Pt-Fe ont porté sur leurs inclusions riches en Os. Le rapport est semblable de la bordure d'un grain de MGP à son cœur, ou parmi les inclusions de différents minéraux d'une seule pépite. Aucune variation isotopique a été découverte dans les grains de MGP qui sont zonés. L'absence de hétérogénéité isotopique dans une pépite rend impossible une origine des pépites par mécanisme de faible température. Les valeurs du rapport $^{187}\text{Os}/^{186}\text{Os}$ ne varient que peu, entre 0.99 et 1.12; la plupart des valeurs se situent entre 1.00 et 1.06, et correspondent donc à des valeurs typiques du manteau. Les éléments du groupe du platine seraient donc dérivés essentiellement du manteau, sans contribution importante d'osmium crustal. Les grains de MGP ont été formés dans des massifs intrusifs, qui ont subi un lessivage et une érosion, pour être concentrés dans des alluvions par processus mécaniques. Les données isotopiques concordent avec la présence dans les pépites de lamelles d'exsolution de MGP, la présence d'inclusions d'olivine saine, et l'absence d'inclusions de minéraux xénocristalliques, sans lien avec les roches ultramafiques. Les valeurs du rapport $^{187}\text{Os}/^{186}\text{Os}$ dans une pépite et des MGP d'une chromitite provenant de l'Oural confirment l'hypothèse que la pépite alluvionnaire a son origine dans la chromitite. La forme xénomorphe et la surface sans signe d'abrasion de certaines pépites pourraient tout simplement résulter de leur tenacité et de la proximité de la source ultramafique.

(Traduit par la Rédaction)

Mots-clés: isotopes d'osmium, minéraux du groupe du platine, pépites, graviers alluvionnaires, massifs ultramafiques, type alpin, type Alaska.

INTRODUCTION

Alluvial nuggets of platinum-group minerals (PGM) are historically important. Placers in the USSR and Colombia and, to a lesser extent, in Canada, were the principal source of the PGE through to the first quarter of the 20th century, until the discovery of lode deposits in South Africa and Siberia and the increased efficiency of recovery of the PGE from Ni-Cu sulfide ores in Canada.

The prevailing view on the origin of nuggets of PGM by the mid 1960s was their derivation from ultramafic rocks by weathering and mechanical processes of transportation. This opinion was based

on the studies of placers in the Urals (Betekhtin 1961), at Tulameen, British Columbia (Rice 1947), and at Joubdo, Ethiopia (Molly 1959). Augustithis (1965) introduced the concept that "nuggets of native Pt have been formed in the lateritic soil" capping the Joubdo ultramafic complex. Ottemann & Augustithis (1967) suggested that they were formed "during the process of early alteration or lateritization". The formation of nuggets was believed to have taken place "by element agglutination under a phase of hydration (low temperature) of the ultrabasic rocks". These ideas were later supported by Cousins (1973) and expanded by Cousins & Kinloch (1976) and Stumpfl (1974) to the "chemical accretion" hypothesis. More recently, Bowles (1988) proposed crystallization of PGM in placers. Rounded shapes were ascribed to processes of chemical accretion, and angular and unabraded textures, to the growth of crystals in sediments (e.g., Bowles 1986, Barker & Lamal 1989).

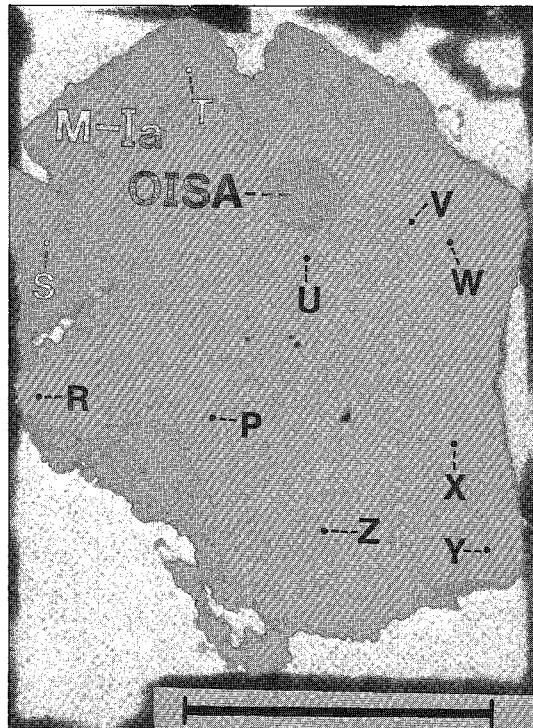


FIG. 1 Back-scattered electron image of osmian iridium nugget from the Atlin district, British Columbia (sample number 10120-11). The osmian iridium, having average composition of $\text{Ir}_{74.6}\text{Os}_{23.8}\text{Pt}_{1.6}$ (Harris & Cabri 1973), contains a round inclusion of Os-Ir-S-As (OISA). The PGM showed evidence of variable concentrations of Os and Re during the Os-isotope analyses. Grey area partially rimming the nugget is an intergrowth of irarsite and osmian iridium (M-Ia in the diagram). The scale bar represents 500 μm . Listed here are $^{187}\text{Os}/^{186}\text{Os}$ ratios (all ± 0.006); the values in parentheses are the correction due to ^{187}Re for the points shown. Z: 1.081 (14.8%), Y: 1.083 (8.7%), X: 1.081 (16.2%), W: 1.083 (9.6 %), V: 1.079 (5.9%), U: 1.078 (8.8%), T: 1.083 (17.5%), S: 1.088 (18.3%), R: 1.082 (9.1%), P: 1.081 (17.5%).

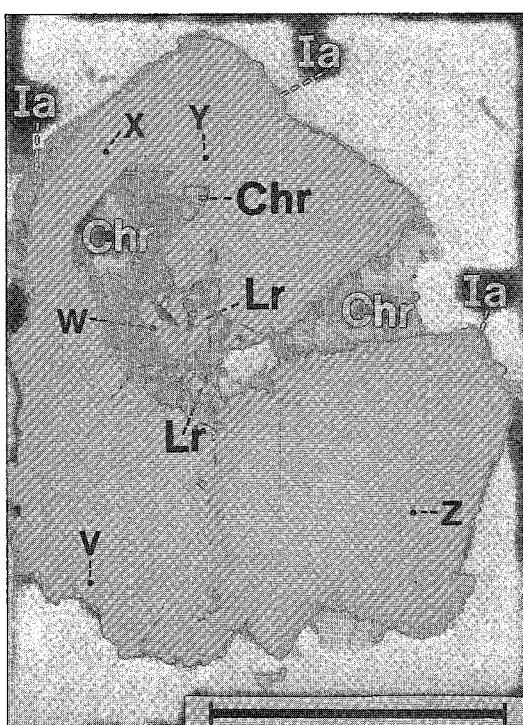


FIG. 2. Back-scattered electron image and $^{187}\text{Os}/^{186}\text{Os}$ values of iridian osmium nugget from the Atlin district, British Columbia (sample number 10120-10). The nugget contains chromite (Chr) and laurite (Lr) and is rimmed by irarsite (Ia). The scale bar represents 500 μm . Listed here are $^{187}\text{Os}/^{186}\text{Os}$ values (all ± 0.006) for the points shown. Z: 1.036, Y: 1.040, X: 1.043, W: 1.036, V: 1.036.

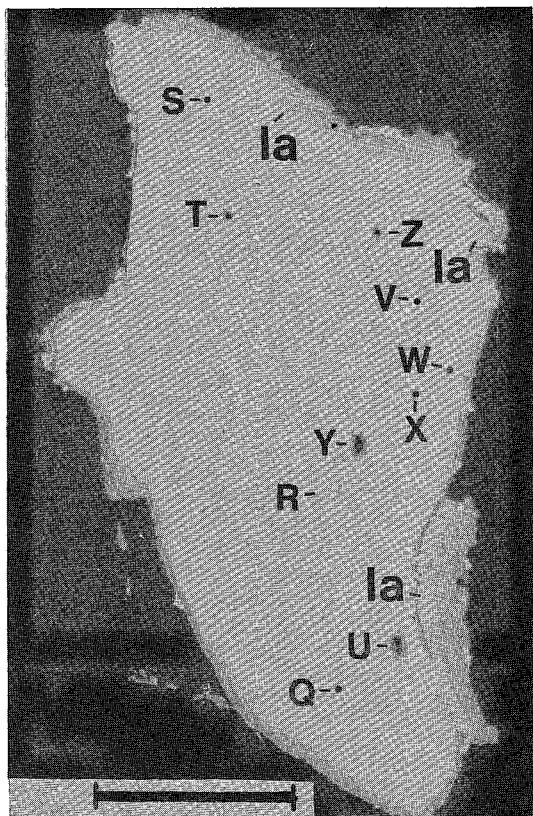


FIG. 3. Values of $^{187}\text{Os}/^{186}\text{Os}$ for an osmian iridium nugget ($\text{Ir}_{59.6}\text{Os}_{36.3}\text{Pt}_{4.1}$, Harris & Cabri 1973) rimmed by irarsite (la) from the Atlin district, British Columbia (sample number 10120-9). The scale bar represents 300 μm . Listed here are $^{187}\text{Os}/^{186}\text{Os}$ ratios (all ± 0.006) for the points shown. Z: 1.064, Y: 1.061, X: 1.066, W: 1.067, V: 1.061, U: 1.064, T: 1.065, S: 1.065, R: 1.060, Q: 1.068.

Mineralogical and petrographic studies supporting the earlier view, mechanical derivation of PGM nuggets from intrusions, include publications by Mertie (1976), Cabri & Harris (1975), Raicevic & Cabri (1976), Cabri *et al.* (1981), Ford (1981), Hagen *et al.* (1990), Johan *et al.* (1990), Nixon *et al.* (1990), and Slansky *et al.* (1991).

Osmium, one of the six PGE, has seven isotopes (^{184}Os , ^{186}Os , ^{187}Os , ^{188}Os , ^{189}Os , ^{190}Os , ^{192}Os); ^{187}Os is the decay product of ^{187}Re , which has a half-life of 4.56×10^{10} years (Luck & Allègre 1983). The $^{187}\text{Os}/^{186}\text{Os}$ ratio of the bulk Earth was 0.805 at 4.55 Ga, and the present ratio is believed to be approximately 1.04 (Allègre & Luck 1980). The values of the mantle have been close to those of

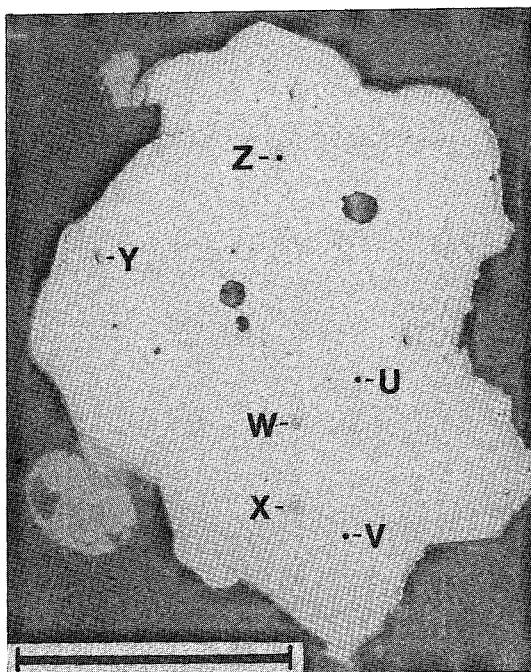


FIG. 4. Back-scattered electron image and $^{187}\text{Os}/^{186}\text{Os}$ values for an iridian osmium nugget of placer origin from Teshio, Japan (sample number = Te-1). The grain showed the highest Re peaks during the Os-isotope analyses, but the Re contents were found to be below the detection limit of an electron microprobe, <0.06 wt.%. The scale bar represents 500 μm . Listed here are $^{187}\text{Os}/^{186}\text{Os}$ ratios (all ± 0.006); the values in parentheses are the correction due to ^{187}Re for the points shown. Z: 1.054 (23%), Y: 1.043 (22%), X: 1.049 (22%), W: 1.052 (24%), V: 1.052 (22%), U: 1.048 (20%).

the bulk Earth because most Os resides in the mantle (Allègre & Luck 1980, Walker *et al.* 1989, 1991a). Crustal rocks, on the other hand, have high and varied Re/Os and $^{187}\text{Os}/^{186}\text{Os}$ ratios, with an estimated average $^{187}\text{Os}/^{186}\text{Os}$ ratio of approximately 30 (Palmer & Turekian 1986, Palmer *et al.* 1988). The large difference in $^{187}\text{Os}/^{186}\text{Os}$ ratios between mantle and crustal rocks makes an isotopic study suitable for examining the contributions from the two sources.

This paper presents $^{187}\text{Os}/^{186}\text{Os}$ ratios of PGM from one lode deposit and a large variety of placers, including samples of residual placer from Joubdo, Ethiopia, which historically generated the controversy on the origin of nugget formation. Models for the formation of PGM nuggets are discussed in the light of the Os-isotope data.

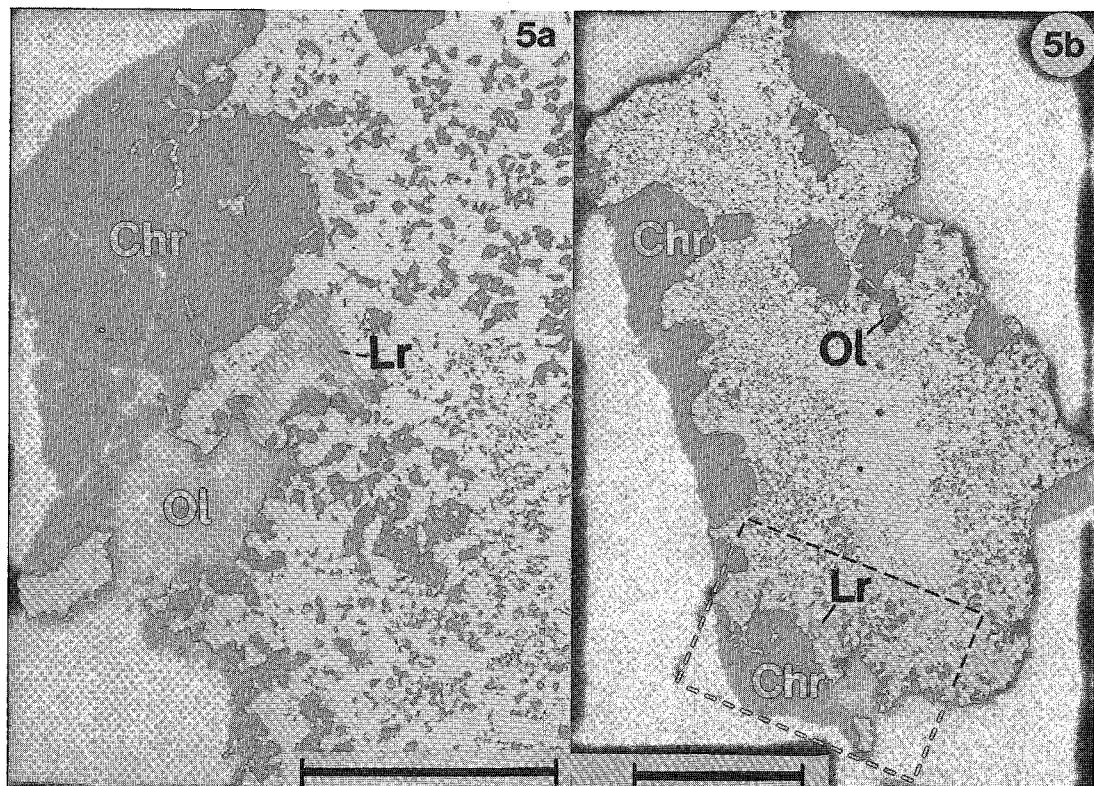


FIG. 5. Back-scattered electron image of isoferroplatinum nugget from Tulameen, containing chromite (Chr), olivine (Ol; Fo₉₃₋₉₅; Nixon *et al.* 1990), laurite (Lr) and iridian osmium inclusions (sample number C-236). Several thin lamellae of iridian osmium (Ir_{21.7}O_{74.7}Ru_{3.5}; Nixon *et al.* 1990) are present in the field shown in Figure 5b, but are not apparent in the photo. The dashed area in Figure 5b (scale bar: 1 mm) is shown in Figure 5a (scale bar: 500 µm). The laurite in the field has ¹⁸⁷Os/¹⁸⁶Os ratios of 1.087 ± 0.008. Other Os-isotope measurements from this nugget are: iridian osmium: 1.092 ± 0.008, iridian osmium: 1.083 ± 0.006, iridian osmium: 1.088 ± 0.006, laurite: 1.077 ± 0.007.

SAMPLE DESCRIPTION

The placer PGM associated with Alpine-type intrusions used in this study come from Atlin, Ruby, Bullion and Cariboo (British Columbia), Adamsfield (Tasmania), and Teshio and Onnebetsu (Hokkaido, Japan). Most Alpine-type samples consist of Os-Ir-Ru alloys. These alloy samples were used for the Os-isotope analyses. The nuggets vary in shape from rounded (Figs. 1, 2) to angular (Figs. 3, 4). They commonly show chemical heterogeneity and zonation, with variable Os and Ru contents (Cabri & Harris 1975). Some nuggets are mixtures of different PGM (Figs. 1, 2), and some are coated by irarsite (Figs. 2, 3, 4) or by a mixture of fine-grained irarsite and Os-Ir alloys (Fig. 1).

Samples associated with Alaskan-type ultramafic intrusions are from Tulameen (British Columbia), Choco (Colombia), Omutnaya River and the Nizhni Tagil dunite massif in the Urals (Russia), Joubdo (western Ethiopia) and Goodnews Bay (Alaska). Most Alaskan-type samples consist of a Pt-Fe alloy, either isoferroplatinum or tetraferroplatinum. The shape of the nuggets varies from well rounded (Figs. 5, 6) to irregular with branches (Fig. 7). The grains of alloy commonly contain inclusions and lamellae of Os-Ir alloys (Figs. 5, 6, 7, 8), laurite and erlichmanite (Figs. 5, 6, 8). These inclusions were used for the Os-isotope study. Chemical zonation, similar to that observed in grains of Os-Ir-Ru alloys from the Alpine-type samples, also is observed in the included phases (Fig. 6).

METHODOLOGY

Analytical procedures

Osmium-isotope ratios were determined on Au-coated PGM grains using a Cameca 3f ion microprobe at MIT. Masses 185, 186, 187, 188 and 189 were determined in order to correct the ratios of $^{187}\text{Os}/^{186}\text{Os}$ for the contribution of ^{187}Re , hydrides and mass fractionation. Some grains displaying high Re peaks required Re corrections of up to 24%, *i.e.*, 24% of mass 187 was contributed by ^{187}Re (Fig. 4). Some showed a heterogeneous distribution of Re. After the correction for Re, calculated $^{187}\text{Os}/^{186}\text{Os}$ values were found to be consistent within the grain (Figs. 1, 4), confirming that the Re correction does not introduce additional uncertainty into the measurements. Replicate analyses of the same grains, made over a 10-month period, show a reproducibility (2σ) of $\pm 0.6\%$. The precision of each result thus is given as $\pm 0.6\%$ or the in-run error, whichever is larger. Detailed operating conditions and reproducibilities of the analyses are described by Hattori *et al.* (1991).

Because significant amounts of Re were noted in several samples during the Os-isotopic analyses, the Re contents were checked on the grains coated with carbon by counting the $\text{Re}L\alpha$ peak for 60 s using the wavelength-dispersion spectrometer on a JEOL 733 electron-microanalyzer system. The operating conditions were 20 kV with a beam current of approximately 25 nA. Several grains of isoferroplatinum and of Os-Ir-Ru alloys were subjected to the examination of Re contents, including an iridian osmium grain that displays the highest Re signals recorded in the ion microprobe (Fig. 4). The $\text{Re}L\alpha$ peak was calibrated on a pure Re metal standard, but it was not detected on any of the grains during the 60 s counting time. Therefore, Re contents are below the minimum detection level for the electron microprobe, 0.06 wt. %.

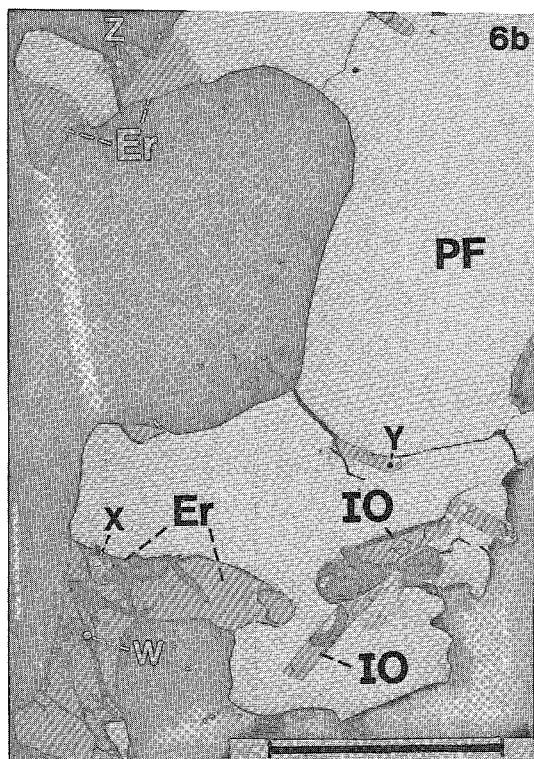
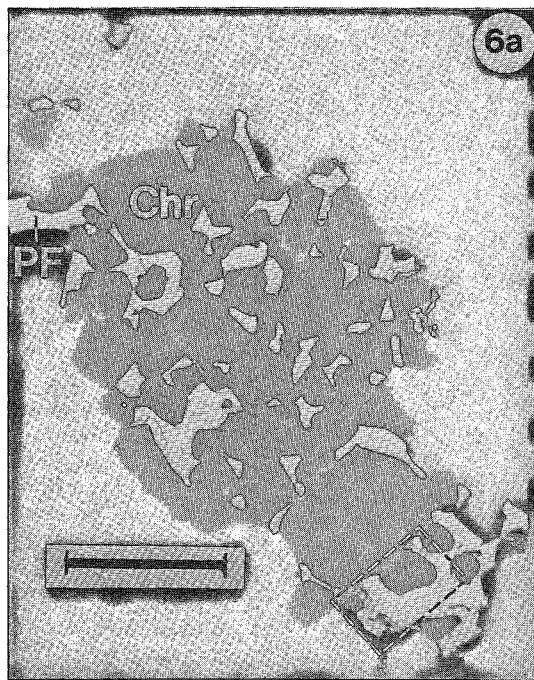


FIG. 6. Back-scattered electron images of isoferroplatinum (PF) nugget with inclusions of chromite (Chr), iridian osmium (IO) and erlichmanite (ER) from Goodnews Bay (sample number GDN-1). Dashed square in Figure 6a (scale bar: 1 mm) is the area shown in Figure 6b (scale bar: 200 μm). Note zonation from an Os-rich core to a Ru-rich rim in erlichmanite. Values of $^{187}\text{Os}/^{186}\text{Os}$ (all ± 0.006) are: Z (erlichmanite): 1.046, Y (iridian osmium): 1.034, X (erlichmanite): 1.030, W (erlichmanite): 1.034.

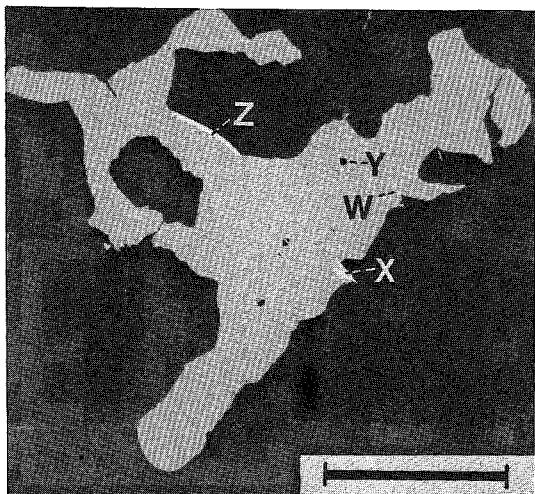


FIG. 7. Irregularly shaped Pt-Fe alloy from Goodnews Bay containing iridian osmium platelets (light color) (sample number 14NMA-NM4). The scale bar represents 1 mm. Values of $^{187}\text{Os}/^{186}\text{Os}$: Z (tabular iridian osmium): 1.104 ± 0.007 , Y (tabular iridian osmium): 1.111 ± 0.008 , X (lamellar iridian osmium): 1.119 ± 0.008 , W (thin rod of iridian osmium): 1.121 ± 0.007 .

Re-Os isotope systematics

The $^{187}\text{Os}/^{186}\text{Os}$ ratio of mantle-derived rocks (Walker *et al.* 1989, 1991a) and the chondrite values (Allègre & Luck 1980) define the range of $^{187}\text{Os}/^{186}\text{Os}$ values of the mantle during geological time (Fig. 9). Although there are detectable variations in $^{187}\text{Os}/^{186}\text{Os}$ ratio in the mantle at a given time, the differences are small compared with the variations in crustal rocks (Figs. 9, 10).

Ultramafic rocks have a low Re/Os ratio (*e.g.*, Walker *et al.* 1988), and the change in $^{187}\text{Os}/^{186}\text{Os}$ ratio over geological time is relatively small. However, the $^{187}\text{Os}/^{186}\text{Os}$ ratio of other crustal rocks increases rapidly owing to generally low Os and high Re contents in the rocks. For example, the $^{187}\text{Os}/^{186}\text{Os}$ ratio of tholeiitic rocks, with an average Re/Os ratio of 35 (Chou *et al.* 1983), would increase from 1.0 to 3.4 in 100 Ma, and the ratio of a black shale with a Re/Os ratio of 75 (Ravizza & Turekian 1989) would change from 1.0 to 7.7 in 100 Ma. Because rocks of the upper crust generally have a high value of $^{187}\text{Os}/^{186}\text{Os}$, the ratio of dissolved Os in surface waters also should be high.

Initial $^{187}\text{Os}/^{186}\text{Os}$ ratio of the PGM

The Re contents in the PGM studied are less than 0.06 wt.%; the Re/Os ratio of the PGM,

containing on the order of 60% Os, should be less than 0.001. Thus the $^{187}\text{Os}/^{186}\text{Os}$ ratio of an Os-Ir-Ru alloy would increase only by 0.0003 in 500 Ma after crystallization owing to the decay of ^{187}Re . The contribution of radiogenic ^{187}Os , therefore, is not significant for samples of Os-bearing alloy.

The isoferroplatinum nuggets contain inclusions of Os-Ir alloy. Assuming that an isoferroplatinum nugget contains less than 0.06 wt.% Re and 5 wt.%

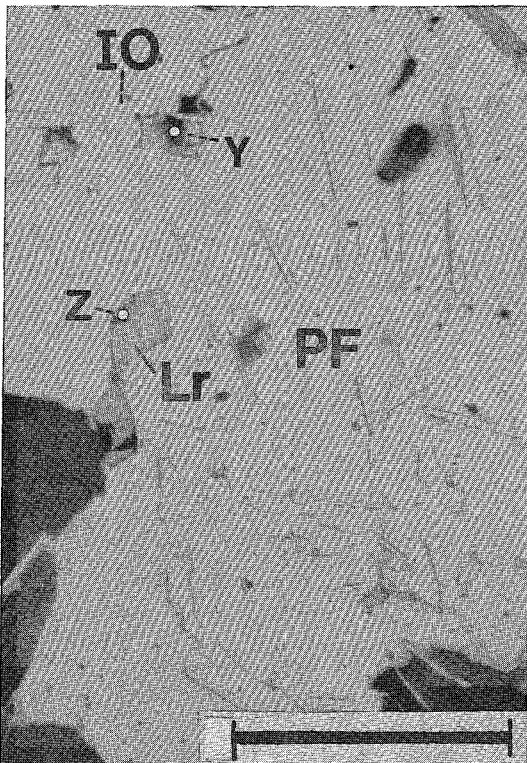


FIG. 8. Photomicrograph of a portion of isoferroplatinum nugget (PF; $\text{Pt}_{74}\text{Ir}_2\text{Fe}_{23}\text{Cu}_1$) containing iridian osmium (IO; $\text{Os}_{66}\text{Ir}_{28}\text{Ru}_3\text{Pt}_2\text{Rh}_1$) and laurite (Lr) inclusions, from the Omutnaya River, Urals (sample number 53). The nugget is rimmed by thin layer of tulameenite. The scale bar represents 500 μm . Values of $^{187}\text{Os}/^{186}\text{Os}$: Z: 1.030 ± 0.012 , Y: 1.021 ± 0.011 . Os-isotope values of different grains of PGM from the nugget include: Os-rich laurite rod: 1.033 ± 0.010 , other end of the laurite rod: 1.040 ± 0.010 , tabular iridian osmium inclusion, B: 1.033 ± 0.009 , tabular iridian osmium inclusion, C: 1.035 ± 0.009 , tabular iridian osmium inclusion, D: 1.037 ± 0.007 , iridian osmium inclusion, E: 1.051 ± 0.010 .

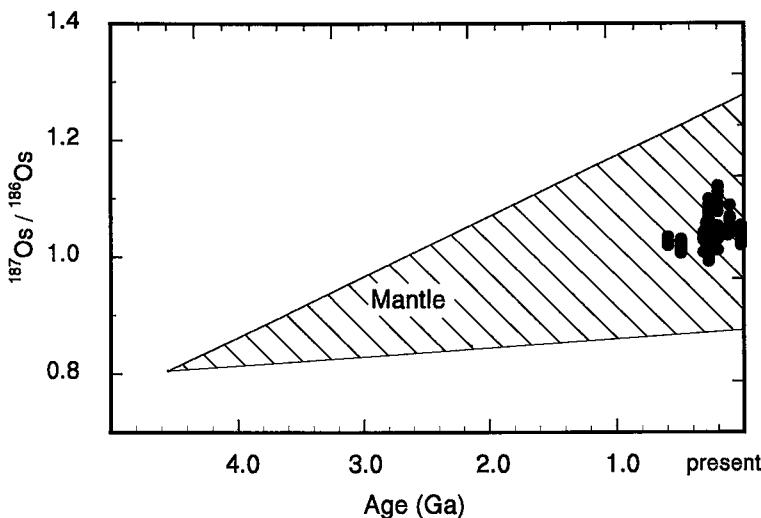


FIG. 9. Values of $^{187}\text{Os}/^{186}\text{Os}$ for the PGM studied compared with the values of the contemporaneous mantle. Solid circles: PGM in this study and data from PGM from Alpine chromitites from Borneo (Hattori *et al.* 1992). The range of mantle $^{187}\text{Os}/^{186}\text{Os}$ values are based on values of chondrite (Allègre & Luck 1980), mantle xenoliths (Walker *et al.* 1989), and komatiite from Gorgona Island (Walker *et al.* 1991a).

Os in inclusions, the $^{187}\text{Os}/^{186}\text{Os}$ ratio of the inclusions would increase by less than 0.003 in 500 Ma. If the inclusions are 0.5 wt.% of the total mass, the increase would be 0.03. The contribution of the radiogenic ^{187}Os must still be small. The observed $^{187}\text{Os}/^{186}\text{Os}$ values are, therefore, safely assumed to be the initial values at the time of their formation.

RESULTS

The $^{187}\text{Os}/^{186}\text{Os}$ ratio of all samples falls in the range from 0.99 to 1.12, with most of the values between 1.00 and 1.06. Several grains that show chemical heterogeneity were examined in detail. Iridian osmium nuggets from the Atlin district (Figs. 1, 2, 3) show variable Os contents, but values of the Os-isotopic ratio were found to be similar within each grain. There is no evidence of overgrowth of PGM enriched in crustal ^{187}Os nor of a trend of ^{187}Os enrichment toward the rim of PGM grains. The Os-isotope ratio of the core and rim of the grains that are coated by irarsite is similar within the limits of precision (Figs. 1, 2, 3), indicating that the alteration of the Os-Ir alloy to irarsite was not accompanied by the introduction of radiogenic Os.

Some nuggets contain several PGM, such as PGE alloys of contrasting compositions and

sulfides. The isotopic ratios of all these PGM, independent of mineral species, are similar (Figs. 5, 6, 7, 8). It is remarkable that, in addition, PGM from widely separated geographic localities also have similar $^{187}\text{Os}/^{186}\text{Os}$ ratios.

The PGM from the Nizhni Tagil dunite massif, Urals, Russia, have an average $^{187}\text{Os}/^{186}\text{Os}$ value of 1.029 ± 0.006 . The value is identical to the average $^{187}\text{Os}/^{186}\text{Os}$ value of 1.035 ± 0.006 for a nugget from the Omutnaya River, Sissertj, near Sverdlosk, Urals, which is located about 180 km to the south. The nugget was derived from the Omutnaya dunite massif, which belongs to the same ultramafic belt as the Nizhni Tagil massif (Beteckhtin 1961).

The data, together with the description of PGM from Joubdo (Ethiopia), appear in Table 1. The rest of the data and description of PGM analyzed are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Canada K1A 0S2.

DISCUSSION

Os-isotope ratios of PGM nuggets

The observed values of $^{187}\text{Os}/^{186}\text{Os}$ from placer PGM (0.99 to 1.12) show a narrow spread, and they are generally lower than the $^{187}\text{Os}/^{186}\text{Os}$ values

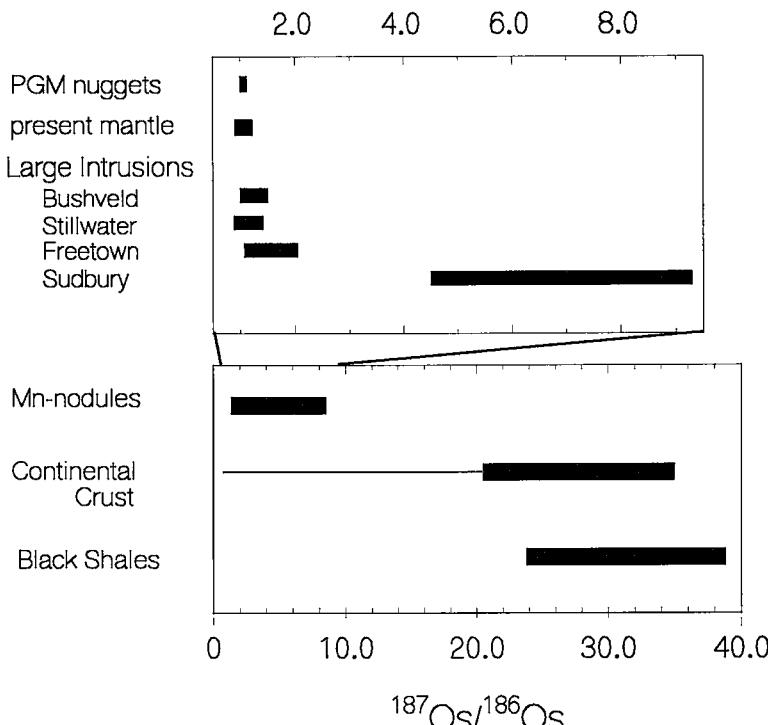


FIG. 10. Values of $^{187}\text{Os}/^{186}\text{Os}$ for the PGM nuggets studied compared with those of large mafic intrusions and crustal rocks. The $^{187}\text{Os}/^{186}\text{Os}$ values of the mafic intrusions are initial values. The values of sediments and manganese nodules are present-day measured values. Sources of data: PGM nuggets (this study), present mantle (Walker *et al.* 1989, 1991a, Martin 1991), Bushveld Complex (Hart & Kinloch 1989), Stillwater Complex (Lambert *et al.* 1989, Martin 1989), Freetown Complex (Hattori *et al.* 1991), Sudbury Complex (Walker *et al.* 1991b), manganese nodule (Luck & Turekian 1983, Palmer & Turekian 1986, Esser & Turekian 1988), continental crust (Palmer & Turekian 1986), Paleozoic black shale (Ravizza & Turekian 1989).

reported for the rocks and grains of PGM from large intrusions (0.88 to 7.55) such as the Bushveld (Hart & Kinloch 1989), Stillwater (*e.g.*, Lambert *et al.* 1989, Martin 1989), Freetown (Hattori *et al.* 1991) and Sudbury complexes (Walker *et al.* 1991b; Fig. 10). The higher values for the large intrusions are attributed to contamination of the magmas by crustal Os.

The $^{187}\text{Os}/^{186}\text{Os}$ values of the PGM nuggets fall within the range of $^{187}\text{Os}/^{186}\text{Os}$ values of the mantle (Figs. 9, 10). The low $^{187}\text{Os}/^{186}\text{Os}$ values of the nuggets suggest that the PGE in the nuggets were derived from the mantle without a significant contribution from crustal Os.

MODELS FOR THE FORMATION OF PGM NUGGETS

Formation of PGM by high-temperature hydrothermal processes

Oxygen- and hydrogen-isotope studies of many epizonal intrusions suggest that the emplacement of igneous rocks in shallow levels commonly results in large-scale meteoric hydrothermal activity (*e.g.*, Taylor & Forester 1979). The presence of fluid inclusions in PGE-rich dunite pipes from the Bushveld Complex seems to support the involvement of a high-temperature ($>700^\circ\text{C}$) fluid for PGE mineralization in large intrusions (*e.g.*,

TABLE 1. $^{187}\text{Os}/^{186}\text{Os}$ RATIOS OF PGM IN RESIDUAL PLACER NUGGETS FROM THE JOUBDO ULTRAMAFIC COMPLEX, BIRBIR DISTRICT, WESTERN ETHIOPIA

Sample	Phase ^(a)	$^{187}\text{Os}/^{186}\text{Os}$
BM1928-247-10	(isoferroplatinum with irregular surface with branches, 2.5 mm x 1 mm, containing abundant oriented iridian osmium lamellae, ~10 μm wide, and tabular iridian osmium. Rims of some iridian osmium inclusions are partially replaced by unidentified Ir-rich phases)	
	tabular iridian osmium grain A in the nugget	1.022 ± .006
	tabular iridian osmium grain B in the nugget	1.022 ± .006
	iridian osmium lamellae	1.027 ± .006
BM1928-247-12	(Pt-Fe alloy with very irregular surface, 0.8 mm x 1.3 mm, containing rod shaped iridian osmium metal, 10 μm x ~200 μm and rounded iridian osmium inclusion)	
	iridian osmium rod inclusion	1.027 ± .006
BM1928-247-13	(rounded Pt-Fe alloy, 0.7 mm, containing short rods of osmium, 20 μm x ~60 μm , and round osmium metal inclusions)	
	iridian osmium rod	1.023 ± .006
	rounded iridian osmium inclusion	1.022 ± .006
BM1928-247-14	(rounded isoferroplatinum nugget containing genkinite, $\text{Pt}_{2.9}\text{Pd}_{1.4}\text{Rh}_{0.4}(\text{Sp}_{2.9}\text{Bi}_{0.02})^{(b)}$ and blebs of fine iridian osmium of 10 μm , and two rods of iridium osmium, 40 μm x 55 μm)	
	iridian osmium rod in the centre of the Pt-Fe,	1.034 ± .008
	iridian osmium rod in the margin of the nugget Pt-Fe	
	30 μm x 70 μm	
	iridian osmium thin lamellae	1.023 ± .007
	iridian osmium rod in the other margin of the nugget	1.019 ± .010
	iridian osmium in the central part of the nugget	1.022 ± .007

(a) Following the nomenclature of Harris & Cabri (1991).

(b) Analytical data given in Cabri et al. (1981).

Stumpfl & Rucklidge 1982, Schiffries & Skinner 1987). Fluids derived from hydrous magmas were involved in the PGM mineralization in the Alaskan-type intrusions near Fifeild, Australia, according to Johan *et al.* (1989). It is, however, unlikely that the relatively small Alpine- and Alaskan-type ultramafic intrusions generated meteoric-hydrothermal activity. Alpine-type intrusions are believed to be either obducted slices of upper mantle or cumulates of boninitic magmas solidified in the lower crust (*e.g.*, Serri 1981). The origin of Alaskan-type intrusions is controversial, but the dunite bodies are considered to represent cumulates formed in the feeder part of arc magmas (Conrad & Kay 1984) or pre-existing Alpine-type ultramafic intrusions (Kelemen & Ghiorso 1986). In either case, there was little opportunity for them to produce hydrothermal activity at an upper crustal level.

Postulated high-temperature hydrothermal activity should have altered the primary silicate chemistry, if such fluids were responsible for much of PGM crystallization. However, pristine silicate mineralogy common in most Alaskan-type intrusions counters this hypothesis. Furthermore, olivine enclosed in PGM has identical compositions to the olivine in chromitites, but distinct from olivine in the rest of intrusions (*e.g.*, Ford 1981, Nixon *et al.* 1990).

In addition, the occurrence of PGM confined within ultramafic bodies and their absence outside ultramafic bodies indicate that the postulated hydrothermal activity did not take place on a large scale. If the hydrothermal activity involved country

rocks, the mineralization of PGE would have also occurred outside the intrusive bodies.

$^{187}\text{Os}/^{186}\text{Os}$ ratios of PGM obtained in this study also suggest that the contribution of crustal Os was insignificant. Though current data and evidence cannot reject the possible involvement of high-temperature fluids in the Alaskan- and Alpine-type intrusions, the overall evidence indicates that hydrothermal activity in the case of these intrusions was not significant in the formation of PGM.

Formation of PGM during serpentinization

Platinum and Pd are considered to be more soluble in hydrothermal fluids compared with the rest of PGE (Mountain & Wood 1988). The lack of variation in Pt and Pd contents during the serpentinization of ultramafic rocks (*e.g.*, Ross & Keays 1979, Oshin & Crocket 1982) suggests that the less soluble Os would not be mobile during serpentinization processes.

Many Alaskan-type intrusions presently display pristine compositions of the primary minerals, including olivine and clinopyroxene, beneath the weathered zones. Examples include the Goodnews Bay complex (*e.g.*, Southworth & Foley 1986), the Tulameen complex (Findlay 1969), and several zoned complexes in the Urals (Betekhtin 1961). On the other hand, Alpine-type intrusions have commonly undergone extensive serpentinization. If serpentinization is responsible for the formation of nugget PGM, one would expect to observe Pt- and Pd-bearing nuggets associated with highly serpentinized Alpine-type intrusions, because Pt and Pd

are more soluble than the other PGE. Empirical observations, however, suggest that relatively unserpentinized Alaskan-type intrusions are accompanied mostly by nuggets of Pt- and Pd-bearing phases, whereas highly serpentinized Alpine-type ultramafic intrusions are associated with Os-Ir-Ru alloy nuggets (e.g., Cabri & Naldrett 1984). Some Alpine-type intrusions are associated with Pt-bearing nuggets as well as Os-Ir-Ru phases (Burgath 1988), but these cases are not common. These observations appear to suggest that the nugget-sized PGM were not formed by the hydrothermal activity that caused serpentinization.

As mentioned earlier, Re/Os values of ultramafic rocks are low compared with those of many other crustal rocks. The values, however, vary within ultramafic rocks and should be very low in chromitites because of their high Os contents (e.g., Crocket 1981, Table 2). This implies that silicates in ultramafic rocks have high Re/Os values. Therefore, radiogenic ^{187}Os should be released during the breakdown of silicate minerals, resulting in high $^{187}\text{Os}/^{186}\text{Os}$ in serpentinizing fluids. If PGM were indeed formed during serpentinization, high $^{187}\text{Os}/^{186}\text{Os}$ values should be observed in some nuggets, but the lack of such evidence precludes serpentinization as the principal process of the formation of PGM.

Tulameenite and some Cu-Pt phases, which commonly rim PGM nuggets, are considered to have been formed during serpentinization (Betekhtin 1961, Nixon *et al.* 1990, Cabri & Genkin 1991). Owing to the low concentration of Os in these minerals, Os-isotopic measurements were not possible during this study. However, these minerals may record a $^{187}\text{Os}/^{186}\text{Os}$ ratio higher than that in the early-formed PGM.

Formation of PGM at low temperatures during weathering or sedimentation

This model includes the formation of PGM nuggets by "element agglutination" (Augustithis 1965) or "accretion" of fine particles (Cousins 1973, Cousins & Kinloch 1976), and their formation by dissolution and precipitation processes (Bowles 1986, 1988, Barker & Lamal 1989). The model may be discounted on two different grounds: mineralogical and textural evidence and geochemical data, including Os-isotope values obtained in this study.

Mineralogical and textural evidence: Some Pt-Fe nuggets contain inclusions of igneous silicate minerals and oxides, exsolution lamellae of other PGM, and sulfides (Figs. 2, 5, 6, 7, 8). Olivine and sulfides are not stable during weathering and sedimentary processes. Their presence indicates that

they were protected by the Pt-Fe alloys during sedimentary processes.

The occurrence of crystallographically oriented lamellae of Os-Ir alloys in Pt-Fe alloys also is difficult to account for by the postulated formation of PGM at low temperatures. The texture is attributed to exsolution of a once-homogeneous alloy at high temperatures (Cabri *et al.* 1981, Slansky *et al.* 1991).

None of the nuggets in our study contain inclusions that are foreign to ultramafic rocks (e.g., Nixon *et al.* 1990). If the nuggets were indeed formed by element "agglutination" or accretion of fine particles in sediments, it is statistically reasonable to assume that the nugget matrix would enclose minerals from adjacent lithologies and minerals abundant in placers, such as quartz, zircon, and monazite. The lack of such foreign inclusions also is consistent with the high-temperature formation of the nuggets.

PGM nuggets consist of crystallographically and compositionally distinct mineral species; they are not noncrystalline, "amorphous" mixtures of metals. The phases observed in the nuggets are isoferroplatinum (cubic Pt₃Fe), tetraferroplatinum (tetragonal PtFe), hexagonal osmium, ruthenium and rutheniridosmine, and cubic iridium. Some form euhedral to subhedral crystals. These nuggets are very different from "minute" "colloform" aggregates of native platinum documented by Wagner and Schneiderhöhn (cited in Wagner 1929). The noncrystalline aggregates are believed to have been formed during weathering of Pt- and Pd-bearing sulfides at low temperatures (Wagner 1929).

Geochemical evidence: Laboratory experiments and thermodynamic calculations demonstrate that PGE may be significantly soluble in acidic saline solutions, even at low temperatures (e.g., Mountain & Wood 1988). Surface waters in ultramafic terranes cannot dissolve a significant amount of PGE because they usually are alkaline ($\text{pH} > 10$) owing to serpentinizing reactions of silicate minerals (e.g., Barnes *et al.* 1978). Surface run-off may become acidic upon completion of serpentinization. This is not the case, however, for most Alaskan-type intrusions, because serpentinization rarely is pervasive.

If "agglutination" were involved in the formation of nuggets of PGM, nuggets would be expected to show isotopic heterogeneity within individual grains because they would contain PGM formed from PGE derived from different parts of an ultramafic intrusion or from different intrusions.

Lack of isotopic heterogeneity in individual grains also rejects consideration of the "agglutination" hypothesis as the principal process for nugget formation.

If the nuggets were precipitated in sediments from dissolved PGE, they would show high and varied $^{187}\text{Os}/^{186}\text{Os}$ values. They would have incorporated ^{187}Os released from decomposing silicate and sulfide minerals of the ultramafic rocks and the accompanying gabbros and volcanic rocks. In addition, dissolved Os in surface waters would not necessarily have a constant $^{187}\text{Os}/^{186}\text{Os}$ ratio. If the nuggets grew by overgrowth on pre-existing PGM grains, the margins should be high in ^{187}Os . One would expect a zoned profile in $^{187}\text{Os}/^{186}\text{Os}$ ratio. The lack of a high ^{187}Os content in the rim or in any nuggets precludes the low-temperature growth of nuggets of PGM as the principal process of their formation.

CONCLUSIONS

The $^{187}\text{Os}/^{186}\text{Os}$ values of PGM within individual nuggets are consistently low and uniform. Some nuggets of PGM show prominent chemical variations, and some consist of different phases, but they are homogeneous in Os-isotopic composition. Low $^{187}\text{Os}/^{186}\text{Os}$ values reject a postulated low-temperature formation of PGM in sedimentary environments. The data indicate that PGE were derived essentially from the mantle without a significant crustal component. PGM were formed in the intrusions, eroded, transported and mechanically concentrated in placers. For eluvial PGM, they remained in the residual soil on ultramafic intrusions during sedimentary processes. The irregular surface of some PGM may simply be attributed to their durable nature and the short distances of transportation of the grains from the source.

This conclusion is in agreement with the mineralogical and petrological studies carried out by Cabri & Harris (1975) and Ford (1981) for nuggets associated with Alpine-type intrusions, and by Raicevic & Cabri (1976), Cabri *et al.* (1981), Hagen *et al.* (1990), Johan *et al.* (1990), Nixon *et al.* (1990) and Slansky *et al.* (1991) for PGM nuggets associated with Alaskan-type intrusions.

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