STRATIFORM AND ALLUVIAL PLATINUM MINERALIZATION IN THE NEW CALEDONIA OPHIOLITE COMPLEX

THIERRY AUGÉ AND PIERRE MAURIZOT

BRGM "Metallogeny and Geodynamics", B.P. 6009, 45060 Orléans Cedex 2, France

ABSTRACT

An unusual type of Pt mineralization has been found in the New Caledonia ophiolite complex, associated with stratiform chromite-bearing rocks at the base of the cumulate series (close to the transition zone between dunite and pyroxene-bearing rocks) and with chromite-rich pyroxenite dykes from the same zone. Two placer deposits, both enriched in Pt, also have been recognized, one derived from the chromite-rich horizons and the other a chromitiferous beach sand of unknown origin. Chromite-bearing rocks are marked by a very strong enrichment in Pt relative to the other platinum-group elements (PGE), with a maximum concentration of 11.5 ppm (average 3.9 ppm). The Pt enrichment takes the form of platinum-group minerals (PGM) included in chromite crystals and is interpreted as being primary. The following minerals have been identified: Pt–Fe–Cu alloys (isoferroplatinum, tulameenite, tetraferroplatinum and undetermined phases), cooperite, laurite, bowieite, malanite, cuprorhodsite, unnamed PGE oxides, and base-metal sulfides with PGE in solid solution. The associated placers show a slightly different mineral association, with isoferroplatinum, tulameenite, and rare cooperite, sperrylite, Os–Ir–Ru alloys and PGE oxides. A more complex paragenesis has been identified in the beach sand, with isoferroplatinum, cooperite, laurite, erlichmanite, Os–Ir–Ru alloys, bowieite, irarsite, hollingworthite, sperrylite, stibiopalladinite, and unnamed Rh sulfide, Pt–Ru–Rh alloy and PGE oxides. This type of mineralization, which differs markedly from the Os–Ru–Ir mineralization previously recognized in podiform chromitite in New Caledonia, shows several analogies with Alaskan-type PGE mineralization. The host chromitite, with typical cumulus textures, is marked by Ti and Fe^{3+} enrichment due to derivation from an evolved liquid. The PGM have crystallized directly from the melt before being trapped by chromite. Precipitation of the Pt–Fe alloys was facilitated by a low fugacity of sulfur. The presence of the PGM in the melt has induced chromite crystallization, facilitating nucleation. This episode of chromite and PGE mineralization in the cumulates indicates an unusual event in the evolution of the complex. It may correspond to injections of a new magma (probably of boninitic affinity) into the chamber. PGE oxides have been recognized in the chromitite horizons and in the placer deposits. The formation of these PGE oxides is related to intense lateritization affecting the primary mineralization. Some oxides are the product of oxidation of pre-existing PGM, whereas others seem to have crystallized in laterite. This indicates a certain mobility of the PGE during the lateritic alteration.

Keywords: platinum-group minerals, platinum-group elements, Pt alloys, ophiolite, ultramafic cumulates, chromitite, platinum mineralization, placer, New Caledonia.

SOMMAIRE

Un type inhabituel de minéralisation en platine, associé à des amas de chromite stratiformes, a été découvert à la base de la série des cumulats de la nappe ophiolitique de Nouvelle-Calédonie, à proximité de la zone de transition entre dunite et cumulats à pyroxènes. On trouve également une minéralisation en platine liée à des pyroxénites chromifères formant des dykes recoupant cette même zone. Deux formations alluvionnaires, enrichies en Pt, ont également été étudiées. L'une dérive d'une minéralisation chromifère à Pt, l'autre, formant des sables de plage, n'a pas de source connue. Les roches chromifères sont marquées par un fort enrichissement en Pt (avec une teneur dépassant couramment 10 ppm) par rapport aux autres éléments du groupe du platine (EGP). La minéralisation est due à la présence de minéraux du groupe du platine (MGP) inclus dans les cristaux de chromite et est interprétée comme primaire. On a identifié: alliages Pt–Fe–Cu (isoferroplatine, tulameenite, tetraferroplatine et des phases non déterminées), cooperite, laurite, bowieïte, malanite, cuprorhodsite, des oxydes de différents EGP et des sulfures de métaux de base avec des EGP en solution solide. Le placer dérivant de cette minéralisation reconnue en roche a un contenu en MGP légèrement différent, avec isoferroplatine, tulameenite, et de rares cooperite, sperrylite, des alliages Os–Ir–Ru et des oxydes de divers EGP. La minéralisation en sable de plage montre une paragénèse plus complexe, avec isoferroplatine, cooperite, laurite, erlichmanite, des alliages Os–Ir–Ru, bowieïte, irarsite, hollingworthite, sperrylite, stibiopalladinite et des phases non déterminées (sulfure de rhodium, alliage Pt–Ru–Rh et des oxydes de différents EGP). Ces minéralisations diffèrent de manière significative des minéralisations en Os–Ir–Ru déjà reconnues dans les chromitites podiformes de Nouvelle-Calédonie; par contre, elles montrent des analogies certaines avec les minéralisations décrites dans des complexes alaskéens. Les chromitites hôtes, qui présentent des textures de cumulat, montrent un enrichissement en Ti et Fe^{3+}, traduisant une cristallisation à partir d'un liquide évolué. Les MGP ont directement cristallisé à partir du liquide magmatique, avant d'être inclus dans la chromite.

La précipitation des alliages Pt–Fe a été facilitée par une faible fugacité en soufre. La présence des MGP dans le liquide, en facilitant sa nucléation, a induit la cristallisation de la chromite. Cette minéralisation en chromite – éléments du groupe du platine correspond à une discontinuité dans l'évolution du complexe. On propose qu'elle soit liée à des injections d'un magma non évolué (probablement d'affinité boninitique) dans une chambre contenant un liquide plus différencié. La formation des oxydes de différents EGP est due à l'intense altération latéritique qui affecte la minéralisation primaire. Certains oxydes sont les produits de l'oxydation de MGP préexistants, d'autres ont directement cristallisé en latérite. Ceci atteste une certaine mobilité des EGP au cours de l'altération.

Mots-clés : minéraux du groupe du platine, éléments du groupe du platine, alliage Pt–Fe, ophiolite, cumulats ultramafiques, chromitite, minéralisation en platine, placer, Nouvelle-Calédonie.

INTRODUCTION

Platinum-group minerals, described as "platinum flakes", were first recorded from New Caledonia in 1891 (Pelatan 1891). They were recognized in alluvial samples, with gold and chromite, collected in the Andam River, which drains metamorphic formations of the Central Range. They were ascribed to serpentinites, which were observed as "sheets" in these formations (Glasser 1904). More recently, platinum-group minerals (PGM) have been described as small inclusions trapped in chromite crystals from chromitite and from dunite found in the mantle sequence of the New Caledonia ophiolite nappe. They consist of Os–Ir–Ru alloys, Ru and Os sulfides and Ir–Cu sulfides (Johan & Legendre 1980, Legendre & Augé 1986, Augé 1988). These PGM belong to the mineral assemblages classically found in ophiolitic chromitite (Constantinides *et al.* 1980, Prichard *et al.* 1981, Stockman & Hlava 1984, Talkington *et al.* 1984, Augé 1985, 1986, Cocherie *et al.* 1989, Nilsson 1990, McElduff & Stumpfl 1990). Such mantle-derived chromitite is characterized by a chondrite-normalized pattern of the PGE, *i.e.*, strongly depleted in Pt and Pd, typical of podiform chromitite (Page *et al.* 1982).

Recent descriptions of Pt mineralization in ophiolitic rocks and in placers derived from ophiolites (Prichard *et al.* 1986, Prichard & Tarkian 1988, Burgath 1988, Hagen *et al.* 1990, Corrivaux & Laflamme 1990, Ohnenstetter *et al.* 1991) led us to investigate the potential for PGE concentration in the New Caledonia ophiolite. A geochemical exploration survey, conducted within the framework of a research project on natural resources, and consisting in the collection and analysis of stream sediment, laterite, alluvial concentrate and rock samples for the PGE, led to the discovery of several types of Pt-rich PGE concentrations, unusual in ophiolites. Two of these, the Pirogues River mineralization (where high concentrations of the PGE were recorded in rock, laterite and alluvium) and the Ni Estuary mineralization (where high concentrations of the PGE were found in beach sand) have been the subject of a detailed mineralogical study, the results of which are presented here.

GEOLOGY AND GEOCHEMISTRY OF THE MINERALIZATION

The New Caledonia ophiolite nappe

The ophiolitic nature of the extensive ultramafic rocks covering about 40% of New Caledonia was recognized in 1977 by Aubouin *et al.* The nappe, now discontinuous, was emplaced in the Upper Eocene (Paris *et al.* 1979). It is mainly composed of mantle rocks; three different units can be distinguished: 1) The northern massifs, composed of mantle peridotite, are characterized by the presence of spinel and plagioclase lherzolite and by the abundance of chromite deposits (Moutte 1982, Johan & Augé 1986); 2) The intermediate massifs are composed of harzburgite, with minor dunite and rare small occurrences of chromite. Both the northern and intermediate massifs form klippes scattered along the west coast (Paris 1981). Finally, 3) The "Massif du Sud", forming the southern extremity of the island and covering one third of its surface, is composed of mantle rocks (harzburgite with minor dunite and pyroxenite dykes and small bodies of chromitite), upon which cumulate dunite, wehrlite, pyroxenite and layered gabbro have locally been recognized (Paris 1981). Upper gabbros, sheeted dykes and pillow lava are not present in the New Caledonia ophiolite nappe.

The Pirogues River area

The mineralization of the Pirogues River (Fig. 1) was discovered during the exploration survey. Very high Pt contents were recorded in stream sediments and river deposits. Detailed mapping of the area and sampling of the different rock types facilitated the discovery of the primary mineralization.

The mineralized area corresponds to a transition zone between a unit of massive dunite, interpreted as a basal cumulate, and pyroxene-bearing cumulate. The dunite passes transitionally into wehrlite or cumulus harzburgite, lherzolite and pyroxenite. Gabbro is invariably in tectonic contact with the cumulates. A variety of cumulus textures have been observed in the different rock-types, including coarse-grained
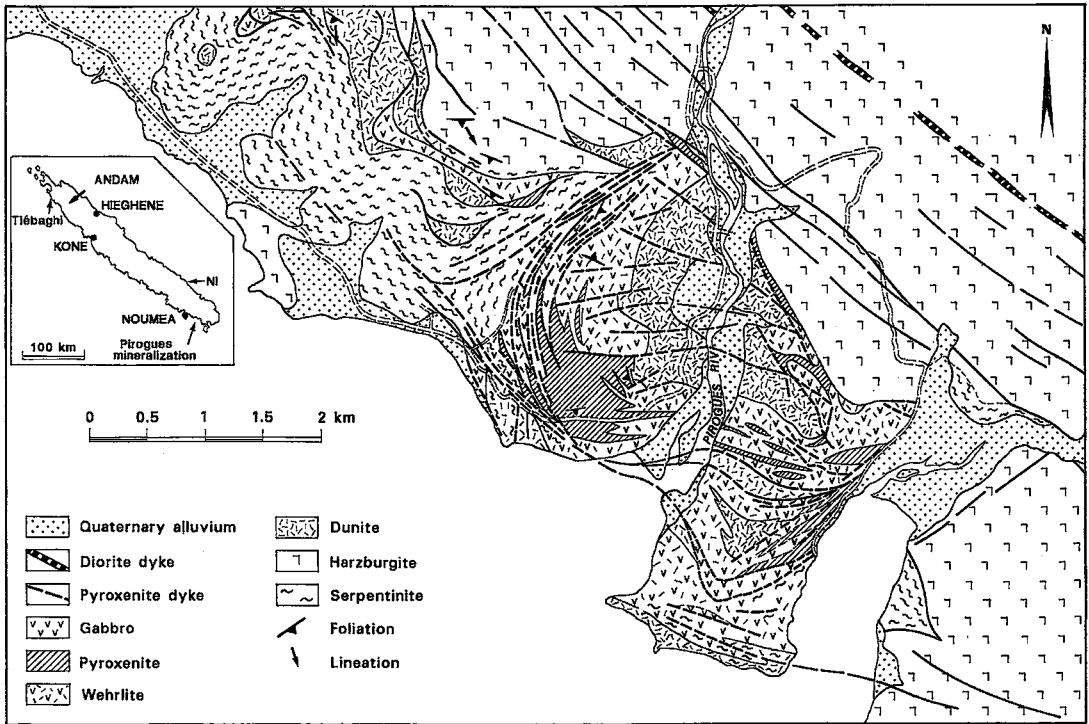
FIG. 1. Simplified geological map of the Pirogues area, New Caledonia.

adcumulate in pyroxenite, and heteradcumulate in wehrlite, with chromite and olivine as cumulus phases.

The basal cumulates are cut by a dense system of dykes consisting of wehrlite, pyroxenite and gabbro up to 10 m thick, which is apparently typical of this area. Composite, multiple-injection dykes also are present. The relationships between the dykes and their host rocks suggest that some of the dykes result from the coalescence of liquid collected from an incompletely crystallized pile of cumulates, by a mechanism similar to filter-pressing. This zone corresponds probably to an active part of the magma chamber, close to a feeder zone.

Chromite concentrations were observed in two different positions. In the dunite and wehrlite cumulates, chromite forms thin schlieren and layers (1 to 10 cm thick and a meter or so long). This type of ore, referred to as "stratiform chromitite", differs distinctly from "podiform chromitite" formed in the mantle sequence (Cassard et al. 1981, Leblanc & Nicolas 1992). It is characterized by euhedral grains of chromite commonly in a pyroxenite matrix. Chromite concentrations also were observed in pyroxenite dykes, where they form either irregular "patches" or layers of disseminated ore (with 10 to 50% chromite crystals) in a pyroxenite matrix, or as irregular concentrations of massive ore, also composed of euhedral crystals

of chromite. In most cases, the chromite is interstitial to large grains of orthopyroxene and clinopyroxene. Chromitite in the pyroxenite dykes has all the characteristics of a cumulate rock, and the term "stratiform chromite" will also be used for this ore, found in the cumulate sequence. It has only been found in the thickest dykes (>1 m). Massive chromitite, without interstitial silicates, was discovered in laterite. This peculiar texture could be the result of weathering of chromitite during lateritization, involving complete removal of the silicates. No concentration of sulfide has been recognized in the mineralized area.

The cumulate sequence is not complete; it is complicated by tectonic imbrication due to its proximity to the base of the nappe. Detailed interpretation of the relationships between the different rock-types is in many places impeded by a thick cover of laterite.

In the zone delimited by a stream-sediment anomaly discovered during the geochemical survey, 93 samples representing the different facies of dykes and cumulates were analyzed for Pt and Pd by lead fire-assay – direct-current plasma – atomic emission spectrometry. Table 1 gives the average and extreme values obtained for the various rock-types. Dunite, wehrlite, pyroxenite and gabbro of the cumulate sequence carry very low Pt values. Slight enrichment can be seen in pyroxenite dykes, with a maximum of

TABLE 1. AVERAGE AND EXTREME Pt AND Pd CONTENTS (IN PPB) IN THE
VARIOUS ROCK-TYPES OF THE PIROGUES SUITE

Formation	Pt	min	max	Pd	min	max
dunite (8)	20	5	43	3	1	7
wehrlite (6)	21	5	40	15	1	65
pyroxenite cumulate (32)	32	5	140	26	2	120
pyroxenite dyke (24)	50	5	200	22	4	70
gabbro (4)	23	5	50	32	5	100
chromitiferous rocks (19)	3882	230	11500	269	12	770

Figure in brackets corresponds to the number of samples analyzed.

200 ppb. The Pd distribution is somewhat different, with very low values for dunite (around 3 ppb), and higher values for the other rocks. The gabbro is richer in Pd than in Pt.

The Pt mineralization seems restricted to the chromite-bearing facies, as all the chromite-rich rocks, either in the pyroxenite dykes or in the cumulates, show Pt enrichment. The Pt content varies between 230 and 11,500 ppb; it is directly related to the Cr_2O_3 content of the rock (Fig. 2), indicating a close association between the Pt carriers and the chromite crystals. The Pd content of the mineralized samples remains relatively low (up to 770 ppb) and shows no correlation with the Pt content.
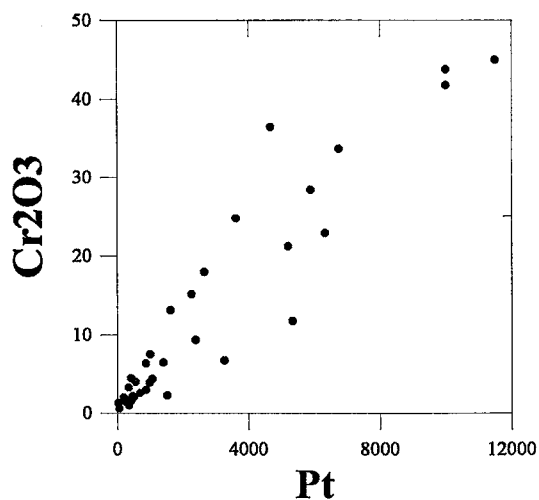
Analyses of the samples with highest Pt contents were made by nickel sulfide fire-assay – inductively coupled plasma – mass spectrometry (Table 2). The results show that Pt is the most abundant PGE, with a ratio Pt/(Pt + Pd + Rh + Ir + Ru) ranging between 4.4 and 7.3, again confirming that Pt plays a major role in the mineralization. The pattern of distribution of the PGE is completely different from that commonly observed in mantle chromitite (Fig. 3). However, the Ir
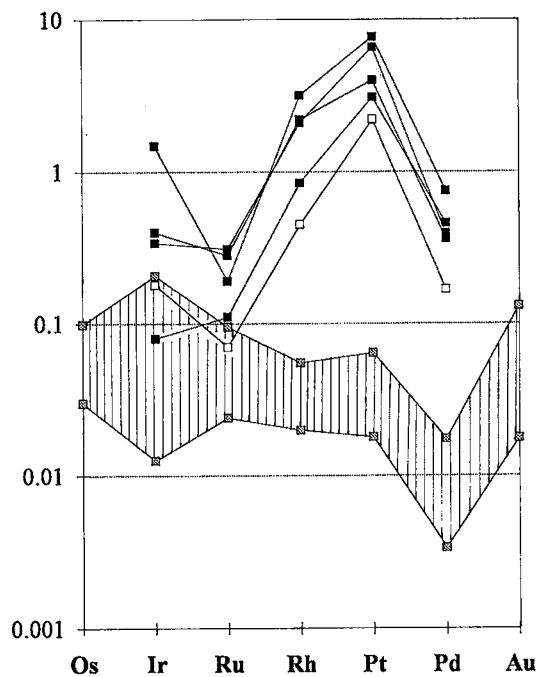

FIG. 2. Correlation of whole-rock Cr_2O_3 (wt.%) – Pt (ppb) in the samples from the Pirogues chromitite, which shows that the PGM are associated with the chromite crystals.

FIG. 3. Chondrite-normalized plots of whole-rock platinum-group elements for the Pt-rich Pirogues chromitite (black square: massive chromite, open square: layered chromite). Hatched area corresponds to compositions of New Caledonia mantle chromitite (T. Augé, unpubl. data).

TABLE 2. PGM AND PGE CONTENT (IN PPM) OF THE PIROGUES CHROMITITE FROM ULTRAMAFIC CUMULATE

N°	Nature	Pt	Pd	Rh	Ru	Ir	Pt alloys	Pt oxides	cooperite	laurite	other
R4	massive chromitite (dyke)	4.61	0.55	0.17	0.11	0.04	2	5	-	4	1
R5	massive chromitite (dyke)	9.81	0.47	0.42	0.31	0.17	5	3	19	1	4
R3	massive chromitite (dyke)	5.94	0.43	0.44	0.28	0.20	4	1	6	3	-
R57	massive chromitite (dyke)	11.50	0.90	0.63	0.19	0.74	5	11	2	2	7
R6	massive chromitite (dyke)	3.90	-	-	-	-	2	1	-	1	4
R1	layered chromitite (cumulate)	3.30	0.20	0.09	0.07	0.09	11	1	9	5	8

and Ru content of the Pt-rich chromitite is within the range of samples of podiform chromitite.

Several heavy-mineral concentrates collected in the area (after washing about 20 liters of gravel) seem to have a high PGE content. One concentrate, collected downstream from the primary mineralization and containing more than 10 ppm Pt, has been studied in detail.

The Ni estuary

High PGE contents were detected in samples of chromitiferous beach sand collected in the Ni Estuary (Fig. 1). The Ni River drains the depleted harzburgite of the Massif du Sud, and there are no indications of the potential source of the alluvial PGE concentration. Chromite crystals on the beach are larger than those normally observed. Systematic sampling of the beach showed that the mineralization is discontinuous and restricted to chromite-rich horizons.

Two samples of sediment, containing respectively 400 and 780 ppb Pt, and very low concentrations of other PGE, were studied.

SAMPLE PREPARATION AND
MICROPROBE TECHNIQUES

Polished sections of chromitite and chromitiferous rocks with high PGE contents were systematically studied in reflected light at a magnification of 200. Base-metal sulfides and platinum-group minerals identified optically were studied with a Cambridge Stereoscan 250 scanning electron microscope (SEM) equipped with a Si(Li) energy-dispersion spectrometer (Tracor Northern TN 2000).

Heavy-mineral concentrates and beach sands were treated in the laboratory to separate the PGM using the technique of Jézéquel (1990). The samples were separated into five grain-size fractions (<50 µm, 50–100, 100–250, 250–500, 0.5–1 mm). Each fraction was separated with a hand magnet into 1) ferromagnetic and 2) para- and non-magnetic. The ten

fractions obtained were then treated with a superpanner in order to separate out the densest particles. The larger PGM obtained were hand-picked and then examined with the SEM and mounted separately in resin to prepare polished sections. For the smaller grain-size fractions, the densest fraction (containing the PGM) obtained with the superpanner was used directly to prepare polished sections of the grains. The PGM in these sections were then identified in reflected light and examined with the SEM.

After the SEM examination, all PGM in rocks and concentrates were analyzed with a Cameca SX50 electron microprobe under the following conditions: acceleration voltage 25 kV, beam current 20 nA, counting time 6 seconds. The standards used were: Cr_2O_3 for Cr, AsGa for As, pyrite for Fe and S, stibnite for Sb, and pure metals for all other elements. The X-ray lines used were $K\alpha$ for Ni, Cu, Fe, S, Co and Cr, $L\alpha$ for Sb, Te, Au, Rh, Ir, Pt and Ru, and $L\beta$ for Os, Pd and As. A PAP correction program was used. Several interferences that could not be avoided (for example, $PdL\beta$ and $AgL\alpha$, or $RuL\beta$ and $RhL\alpha$) were corrected by calculation.

Most analyses of PGM included in chromite crystals revealed the presence of Cr and Fe due to excitation of the matrix, because of the small size of the particle. This explains the low analytical total in some cases. Thus Cr, and the corresponding proportion of Fe due to the chromite (determined from the known Cr/Fe ratio, measured in the host chromite) are generally subtracted from the raw analytical data, and the atomic concentration is calculated from the corrected analytical data.

SAMPLE DESCRIPTION

PGM in chromitite (the Pirogues mineralization)

Six samples with Pt contents ranging between 3.3 and 11.5 ppm were examined. Their characteristics are given Table 2. All the PGM in the six samples occur as inclusions within chromite crystals. Most PGM are included in unaltered and unfractured chromite. Rarely,
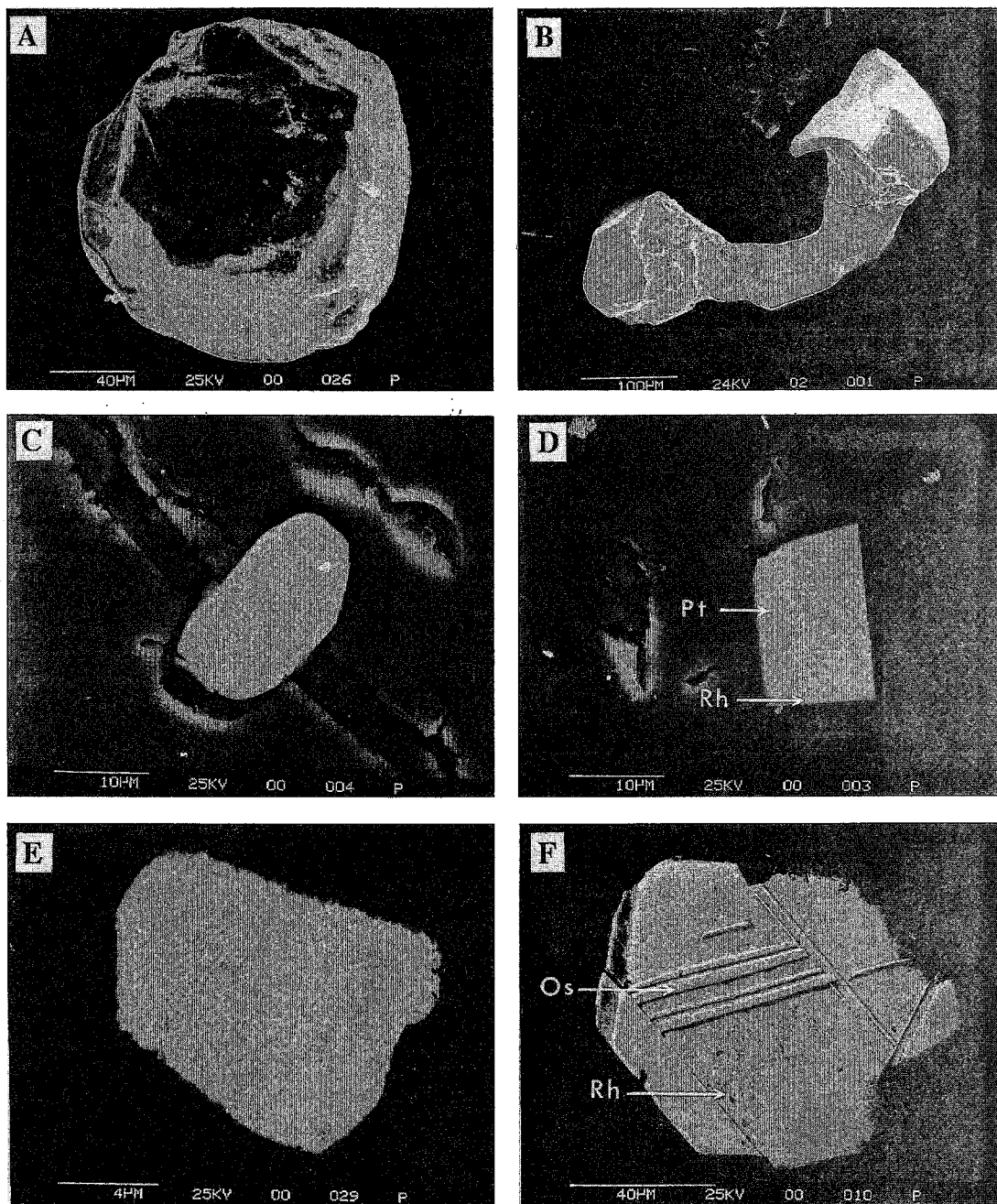
FIG. 4. Scanning electron microscope images of PGM. A. Euhedral grain of isoferroplatinum from the Pirogues mineralized alluvium; B. composite PGM from the Ni mineralized alluvium; C. isoferroplatinum included in chromite crystal; D. euhedral cooperite [Pt], with an attached undetermined Rh sulfide [Rh] in chromite; E. Pt–Fe–Cu alloy containing undetermined needles (images C to E are inclusions in chromite from the Pirogues mineralization); F. euhedral grain of isoferroplatinum containing Os laths [Os] and undetermined Pt–Ru–Rh alloy [Rh] (grain from the Ni alluvium).
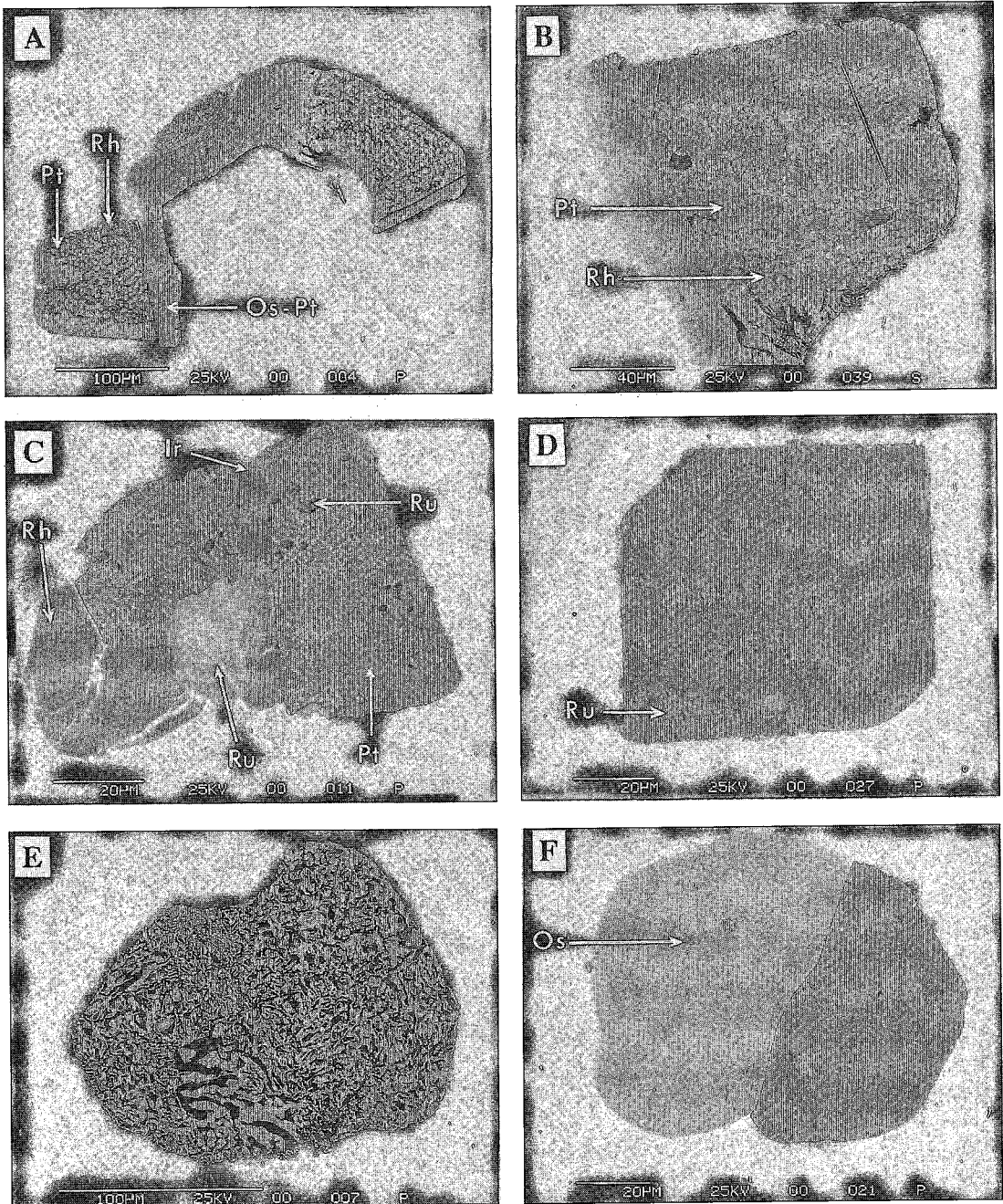
FIG. 5. Scanning electron microscope images of PGM. A. Section of the composite grain shown in Fig. 4B, composed of Pt–Fe alloy [Pt] with undetermined Pt–Ru–Rh alloy [Rh] and "interlayered" Os alloy and Pt alloy [Os–Pt]; B. detail of the grain, showing the relationship between the Pt–Fe alloy [Pt] and Pt–Ru–Rh alloy [Rh]; C. complex grain composed of isoferroplatinum [Pt] containing inclusions of laurite [Ru], a lath of bowieite [Ir], a large zoned grain of laurite [Ru], and an undetermined Rh sulfide [Rh]; D. euhedral grain of isoferroplatinum containing inclusions of laurite [Ru]; E. grain showing isoferroplatinum in a symplectitic association with a mineral that has not been preserved; F. two-phase grain of iridium (white) and erlichmanite (grey) containing inclusions of osmium (Os). All grains are from the Ni mineralized alluvium.

the PGM is found at the boundary between chromite and a silicate inclusion (still mainly enclosed by the chromite grain). In some cases, PGM appear within small cracks related to serpentinization and are obviously not genetically related to them. Rather, the presence of the PGM seems to have controlled the direction of the cracks.

The size of the PGM grains is very variable, from less than 1 μm (too small to be accurately analyzed), up to 200 μm in largest dimension. Most of the grains are in the range 10 to 40 μm (Fig. 4). PGM inclusions are generally single-phase and isometric, but some are composed of two phases, both isometric; others appear elongate (tabular crystals). Aggregates of PGM crystals trapped in chromite also have been observed.

Some grains show intergrowths of two phases, which could be due to exsolution. Others enclose very fine needles that have not been identified (Fig. 4E).

PGM in alluvium

Ninety per cent of the PGM from the Pirogues mineralized alluvium occur in the <100 μm fraction, which represents only 0.1 wt.% of the concentrate. The rest of the PGM are in the 100–250 μm fraction, in which most of the grains are ferromagnetic, whereas only 30% of the grains in the <100 μm fraction is ferromagnetic. About 150 grains from the Pirogues concentrates were separated and studied. In the Ni beach sand, most PGM were in the 50–100 μm fraction (no magnetic separation was done). About 70 grains were studied. Concentrates from both localities are composed mainly of chromite grains, varying in shape from euhedral crystals to rounded and weathered grains. There are also rare iron pisolites and accessory magnetite.

Alluvial PGM are generally euhedral, showing crystal faces; grains from the Pirogues alluvium are generally better preserved than the rounded grains from the Ni mineralized alluvium (beach sand at the Ni Estuary). The largest crystal is 0.4 mm long; the smallest is about 40 μm; most of the crystals have a diameter in the range 100 to 150 μm. In polished section, many grains can be seen to be complex and composite.

Five types of grains have been identified (Figs. 4, 5): 1) euhedral (subhedral and, in rare cases, rounded) monomineralic grains, 2) euhedral grains with small inclusions of other PGM, 3) complex polyphase grains (composed of one major phase, with abundant inclusions and trapped grains, or, in some cases, exsolved minerals), 4) complex grains composed of two phases, one being in symplectitic association with another that has been removed from the grain (Fig. 5E), 5) rhythmically zoned grains. Other textures can be attributed to dissolution due to weathering.

Mineral assemblages

Table 3 summarizes the different mineral species occurring in the chromitite of the Pirogues River and in the Pirogues and Ni mineralized alluvium. Data for mantle chromitite for the Massif du Sud and Tiébaghi massif (New Caledonia) are included for comparison.

In the Pirogues chromitite, the distribution of the PGM varies from one sample to another. Whereas Pt–Fe–(Cu) alloys are systematically present (Table 3), Pt sulfides (cooperite) are irregularly distributed; they are abundant in only three samples, and are lacking in two samples. Pt–Fe oxides were analyzed for the first time (Augé & Legendre 1994); their proportions vary considerably. The main source of Pt in the chromitite appears to be the Pt–Fe alloys and oxides and the Pt sulfides. Laurite also is widespread. Bowieite, malanite and cuprorhodsite were found in three samples of chromitite. Base-metal sulfides containing exsolution bodies of PGM and PGE in solid solution were observed in one sample. Os–Ir–Ru alloys, which are the most common PGM in chromitite from the mantle sequence of the Massif du Sud (Legendre & Augé 1986, Augé & Johan 1988), have not been recorded in the Pirogues chromitite.

The Pirogues mineralized alluvium is also characterized by the abundance of members of the Pt–Fe–(Cu) system, but with a different distribution: isoferroplatinum, rare in chromitite, is the most common PGM (Table 3). Pt–Fe oxides are also abundant in the Pirogues alluvium. The rarity of cooperite and the lack of laurite are noteworthy. On the other hand, Pt arsenide (sperrylite) and separate grains of Os–Ir–Ru alloys, lacking in the chromitite samples, have been discovered in the alluvium.

TABLE 3. PGM DISCOVERED IN THE PIROGUES AND NI SUITES

Mineral name	Pirogues chromitite	Pirogues alluvium	Ni alluvium	M du Sud	Tiébaghi
				mantle chromitite	
Isoferroplatinum Pt3Fe	·	●	●		
Tulameenite Pt2FeCu	·	·			
Undetermined PtFeCu	●				
Unnamed PtRuRh			·		
Unnamed Pt-Fe oxide	●	●	·		
Tetraferroplatinum PtFe	●				
Cooperite PtS	●	·	·		
Iridium IrOsRu		·	●	●	
Osmium OsRuIr		·	●	●	·
Erlichmanite OsS2			·		
Laurite RuS2	●		●	·	●
Unnamed Rh5S4			·		
Bowieite-Kashinite (Rh,Ir)2S3	·		·		·
Irarsite IrAsS			·		
Hollingworthite RhAsS			·		
Malanite (Cu,Fe)(Pt,Rh)2S4	●		·		
Cuprorhodsite (Cu,Fe)(Rh,Ir)2S4	●				
Sperrylite PtAs2		·	·		
Stibiopalladinite Pd5Sb3			·		
Unnamed Pt-Ir-Fe-Rh oxide	·	·			
Unnamed Ir-Fe-Rh oxide		·			
Unnamed Fe-Rh-Pt oxide		·			
Unnamed Ru-Mn-Fe		·			
PGE-bearing BMS	●				

Data for mantle chromitite are from Legendre & Augé (1986) and Augé (1988).
The size of the symbol reflects the frequency of the mineral.

The mineralized alluvium of the Ni Estuary contains the largest number of mineral species. Like the Pirogues alluvium, it is composed mainly of isoferroplatinum. However, numerous alloys of the Os–Ir–Ru series, PGE sulfides (cooperite, laurite, erlichmanite), sulfarsenides (hollingworthite and irarsite) and antimonides (stibio-palladinite) were found, either as small inclusions in other PGM, as separate grains, or as parts of composite grains.

PGE oxides have been recognized in the three mineralized zones. They comprise minerals of the Pt–Fe–O system, with various contents of O, but also more complex Pt–Ir–Fe–Rh oxides and Ru–Mn–Fe oxides (or hydroxides). Their detailed characteristics and the analytical techniques employed were described by Augé & Legendre (1994).

CHEMISTRY OF THE HOST CHROMITITE

The composition of chromite from different samples of Pt-rich chromitite of the Pirogues suite is plotted in Figure 6, together with disseminated chromite from the cumulate series, and chromitite from mantle deposits (Tiébaghi and Massif du Sud). Mantle deposits from the Tiébaghi massif are composed of chromite of very constant composition, with high Cr (55.5–63.5 wt.% Cr_2O_3) and low Al (7.8–14.2 wt.% Al_2O_3), low Fe^{3+} (1.5–4.3 wt.% Fe_2O_3), low Ti (around 0.1 wt.% TiO_2) and a high Mg/(Mg+Fe) ratio (0.60–0.75). Mantle deposits from the Massif du Sud are slightly enriched in Al and impoverished in Cr, as indicated in Figure 6. Chromite concentrations in the cumulate series of the Pirogues area, enriched in Pt, differ significantly from those of samples of mantle chromitite in having relatively low but variable Cr (36.3–49.4 wt.% Cr_2O_3), low Al (8.9–11.3 wt.% Al_2O_3), high Fe^{3+} (10.6–21.2 wt.% Fe_2O_3), high Ti (0.5–0.9 wt.% TiO_2) and a low Mg/(Mg+Fe) value (0.30–0.41). No significant difference was observed between chromitite in dykes and chromitite in cumulates. Chromite in mantle chromitite is characterized by Al-for-Cr substitution, with constant Fe^{3+}, whereas chromite in stratiform chromitite is characterized by Fe^{3+}-for-Cr substitution, with constant Al.

Disseminated chromite in cumulate rocks hosting the mineralization is marked by large compositional variations that overlap the field of the PGE-rich chromitite. The trend of Fe^{3+} enrichment is strongly marked, suggesting crystallization in more oxidizing conditions. The differences in chromite composition between stratiform and podiform deposits indicate that they derive from liquids of very different compositions (Roeder 1994).
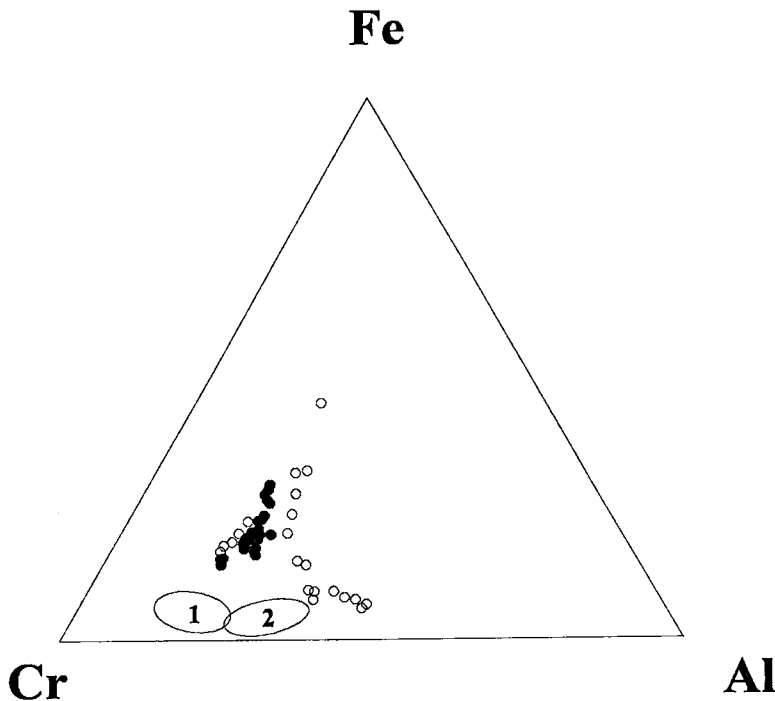

FIG. 6. Composition of chromite from PGE-rich chromitite of the Pirogues mineralization (closed circles) and of disseminated chromite in cumulates hosting the mineralization (open circles). Fields correspond to mantle chromitite from Tiébaghi (1) and Massif du Sud (2) deposits.

THE PLATINUM-GROUP MINERALS

Pt–Fe–(Cu–Pd) phases

Two types of Pt–Fe mineral have been identified: alloys and oxides, both in the chromitite and alluvium. Although the existence of natural Pt oxide had previously been mentioned (Cabri *et al.* 1977, 1981, Loucks 1978, Ixer & Prichard 1989, Nixon *et al.* 1990, Legendre & Augé 1993, Prichard *et al.* 1994), the abundance and the size of the minerals observed here are quite uncommon.

Isoferroplatinum and undetermined Pt–Fe–Cu alloys: Isoferroplatinum represents the majority of the PGM of the Pirogues and Ni Estuary alluvial suites. It generally occurs as euhedral grains, with or without trapped phases (Fig. 5D). In the Pirogues chromitite, isoferroplatinum is rare (only three crystals were identified). Representative compositions of isoferroplatinum are given in Table 4.

The composition of isoferroplatinum from the Pirogues mineralized alluvium is shown in Figure 7A. No significant compositional zoning has been observed, and only slight variations in the Pt/Fe ratio are recorded from one grain to another. In contrast to observations made elsewhere (Augé & Legendre 1992), Cu does not enter in significant amounts into

isoferroplatinum, except in two grains, where it reaches 2.6 wt.%. The Pt content of isoferroplatinum varies between 82.0 and 92.0 wt.% [the latter value corresponds to the pure $Pt_3(Fe,Cu)$ end-member]. The deficiency in Pt is balanced by the incorporation of Pd, as indicated in Figure 8, Pd reaching a maximum of 4.5 wt.%. Isoferroplatinum plots just below the ideal substitution line; the role of other PGE in substitution for Pt is thus minor, and Pt is rarely replaced by Fe or Cu. Iridium, however, enters significantly into isoferroplatinum (maximum 4.7 wt.%), and Rh also is present (up to 2.1 wt.%).

Isoferroplatinum from the Ni mineralized alluvium shows less variation in Pt/Fe (Fig. 7B). Similarly, its Pd content is lower. On the other hand, there is a clear Rh-for-Pt substitution, with a maximum Rh content of 6.1% (Fig. 9). Note that the different compositions plot on the 1:1 substitution line, with only local enrichments in Os, Ru and Ir. Only Cu (average 0.3 wt.%) and Ni (0.1 wt.%) are generally present.

The composition of the Pt–Fe–Cu alloys in the Pirogues chromitite is plotted in Figure 10A. The composition of the Pt–Fe oxides is plotted in Figure 10B. There are two compositional types of Pt–Fe–Cu alloy: a composition close to the Pt_3Fe (with a Pt content of about 88.9 wt.%), and a compositional range from PtFe (with a Pt content of about 62 wt.%) to a composition close to PtFeCu (or Pt_2FeCu, with an excess of Fe).

TABLE 4. SELECTED COMPOSITIONS OF Pt-Fe-Cu, Os-Ir-Ru AND Pt-Ru-Rh ALLOYS

	Isoferroplatinum						Tulameenite		Os-Ir-Ru alloys						PtRuRh alloy	
	AP5	AP7	Ni1	Ni2	R4A	R1D	AP1	AP3	Ni1	Ni4	Ni5	Ni6	Ni8	Ni12	Ni16	Ni17
Weight per cent																
Os	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	61.39	13.15	27.97	41.74	23.58	59.45	2.15	2.22
Ru	0.00	0.06	0.00	0.38	0.12	0.00	0.05	0.00	17.32	0.45	4.69	30.59	8.99	0.99	25.96	25.52
Pt	85.75	91.81	82.02	82.93	78.88	71.20	74.76	75.82	0.99	7.80	5.49	1.30	15.01	1.32	54.16	54.28
Cr	0.02	0.03	0.00	0.00	0.63	1.14	0.13	0.00	0.00	0.01	0.02	0.02	0.12	0.00	0.10	0.05
As	0.07	0.00	0.22	0.00	0.00	0.04	0.04	0.26	0.09	0.10	0.22	0.06	0.00	0.09	0.00	0.00
Ir	4.67	0.35	1.72	0.11	0.13	0.04	2.34	0.29	18.83	78.22	60.83	26.15	49.81	37.53	2.93	3.11
Pd	0.42	0.00	6.81	0.60	5.48	0.94	0.34	0.00	0.00	0.00	0.20	0.24	0.00	0.00	0.00	0.00
Co	0.00	0.02	0.00	0.00	0.03	0.01	0.00	0.00	0.04	0.02	0.00	0.00	0.02	0.00	0.00	0.00
S	0.00	0.01	0.09	0.00	0.00	0.12	0.08	0.03	0.00	0.03	0.00	0.03	0.00	0.00	0.01	0.00
Fe	7.94	7.72	7.96	8.60	11.00	17.19	13.25	9.28	0.39	0.56	0.00	0.00	0.69	0.00	1.19	0.76
Rh	0.56	0.51	0.37	6.07	0.42	0.23	0.27	0.80	0.46	1.61	1.17	0.36	1.55	0.07	13.68	14.00
Cu	0.21	0.12	0.36	0.49	0.82	6.00	8.70	13.24	0.17	0.85	0.57	0.28	0.52	0.40	0.10	0.18
Ni	0.04	0.03	0.07	0.07	1.01	1.99	0.16	0.27	0.11	0.02	0.00	0.06	0.00	0.01	0.04	0.12
Total	99.67	100.65	99.62	99.25	98.51	98.86	100.14	99.99	99.78	102.80	101.15	100.82	100.29	99.99	100.31	100.23
Atomic proportions																
Os	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	52.49	12.30	26.11	32.39	21.19	58.67	1.57	1.64
Ru	0.00	0.09	0.00	0.57	0.17	0.00	0.07	0.00	27.86	0.78	8.24	44.66	15.21	1.83	35.68	35.36
Pt	70.83	75.93	64.39	64.68	59.52	45.73	48.86	49.72	0.83	7.11	5.00	0.98	13.15	1.27	38.57	38.97
Cr	0.05	0.08	0.00	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	0.15	0.00	0.45	0.00	0.00	0.07	0.07	0.45	0.20	0.24	0.51	0.11	0.00	0.24	0.00	0.00
Ir	3.91	0.29	1.37	0.08	0.10	0.00	1.55	0.19	15.93	72.39	56.19	20.08	44.30	36.64	2.11	2.27
Pd	0.63	0.00	9.80	0.86	7.58	1.11	0.41	0.00	0.00	0.00	0.33	0.33	0.00	0.00	0.00	0.00
Co	0.00	0.05	0.01	0.00	0.06	0.02	0.00	0.00	0.11	0.05	0.00	0.00	0.06	0.00	0.00	0.00
S	0.00	0.06	0.45	0.01	0.00	0.46	0.33	0.14	0.00	0.15	0.00	0.15	0.00	0.00	0.04	0.00
Fe	22.90	22.30	21.82	23.43	27.48	36.24	30.25	21.26	1.12	1.77	0.00	0.00	2.11	0.00	2.95	1.90
Rh	0.88	0.80	0.55	8.98	0.61	0.28	0.34	0.99	0.73	2.78	2.02	0.51	2.58	0.13	18.47	19.06
Cu	0.52	0.31	0.87	1.17	1.89	11.82	17.46	26.66	0.45	2.38	1.59	0.66	1.40	1.18	0.22	0.39
Ni	0.12	0.09	0.17	0.19	2.54	4.24	0.35	0.59	0.30	0.05	0.00	0.15	0.00	0.04	0.10	0.29

For minerals included in chromite, raw analyses are given and atomic concentrations are calculated on the base of the corrected analyses.
AP and Ni - minerals from the mineralized alluvium of the Pirogues and Ni zone respectively, R - minerals from the Pirogues chromitite.
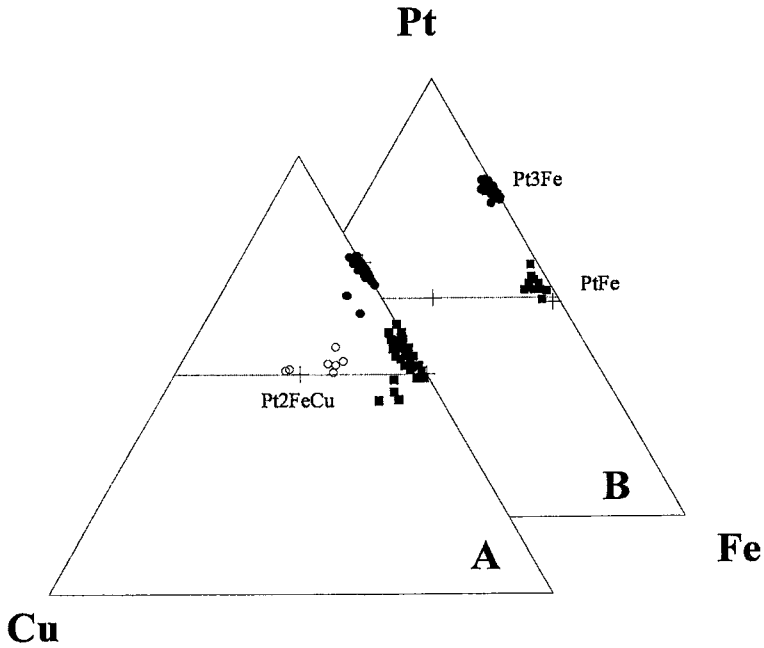
FIG. 7. Composition of Pt–Fe–Cu minerals from the mineralized alluvium. A. Pirogues
(closed circles: isoferroplatinum; open circles: tulameenite; squares: Pt–Fe oxides);
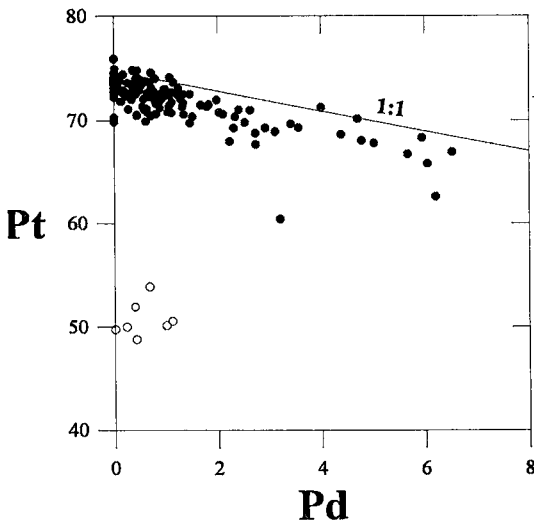B. Ni (closed circles: isoferroplatinum; squares: Pt–Fe oxides).

FIG. 8. Correlation of Pt and Pd (atomic proportions)
in isoferroplatinum (closed circles) and tulameenite
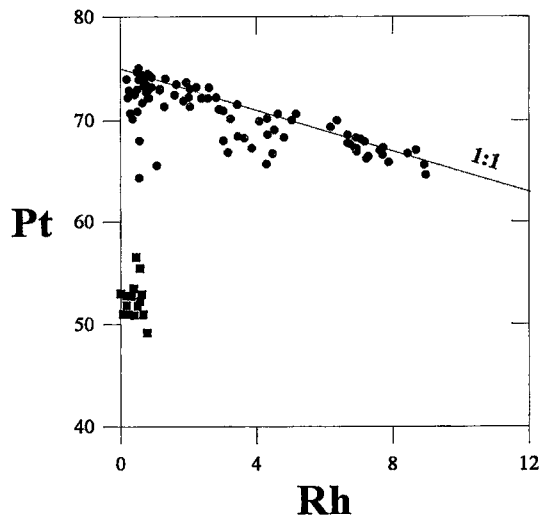(open circles) from the Pirogues mineralized alluvium.

FIG. 9. Correlation of Pt and Rh (atomic proportions)
in isoferroplatinum (circles) and Pt–Fe oxides (squares)
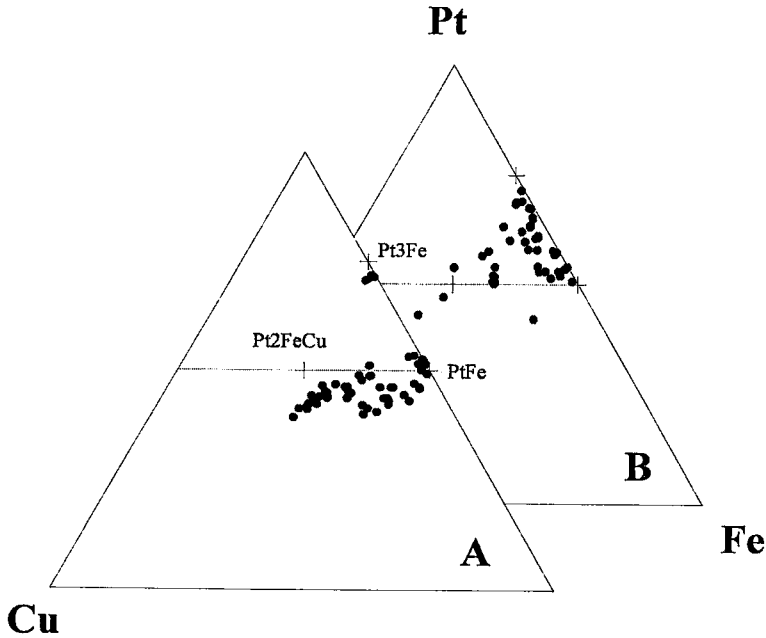from the Ni alluvium.

FIG. 10. Composition of Pt–Fe–Cu minerals. A. Alloys from chromitite, Pirogues mineralization, B. oxides from chromitite, Pirogues mineralization.

Very low contents of Os, Ir, and Ru have been detected in all the Pt–Fe–Cu alloys. Rh and Pd are the only PGE invariably present, but no clear substitution trend of PGE for Pt has been recorded. Cu reaches a maximum value of 17.0 wt.% (Fig. 10A). Figure 11 shows substitution of Cu for Fe, from close to tetraferroplatinum to a composition close to tulameenite (with a deficiency in Pt). However, this result is difficult to interpret, since detailed SEM investigations have shown that most of the Pt–Fe–(Cu) alloys included in chromitite are two-phase PGM, the grains being too small to be correctly analyzed. A Cu-rich phase (tulameenite?) commonly occurs as needles in a Pt–Fe alloy (Fig. 4E). The compositions obtained probably reflect the different proportions of the phases in the volume analyzed. Bowles (1990) suggested the possibility of solid solution between tulameenite and tetraferroplatinum. Observations made here are consistent with low-temperature exsolution for some compositions.

Mineral compositions reveal appreciable differences among localities sampled. Isoferroplatinum from the Pirogues alluvial suite is enriched in Pd, whereas isoferroplatinum from the Ni Estuary suite shows Rh enrichment, both alluvial settings being marked by isoferroplatinum with a low level of Cu. In contrast, the Pirogues chromitite is characterized by the scarcity of isoferroplatinum and the abundance of Cu-rich Pt–Fe alloys. This apparent difference between PGM-rich alluvium and chromitite of the Pirogues River could be

explained in terms of the size of the PGM studied. In the alluvium, isoferroplatinum (Cu-poor) coexists with tulameenite (as discrete grains), whereas in the chromitite mineralization, the intermediate compositions correspond, in most cases, to close associations of tulameenite and Pt–Fe alloy in very small particles.
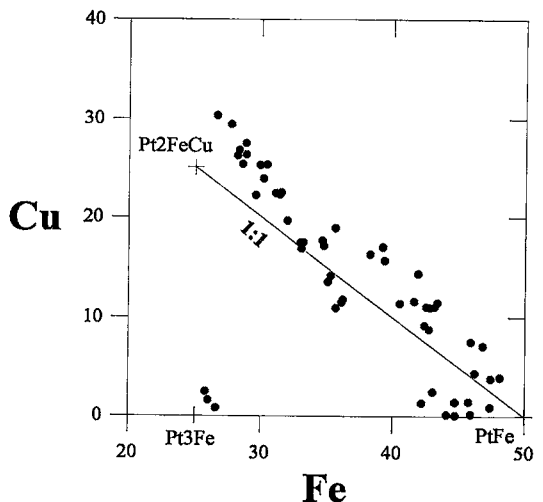

FIG. 11. Correlation of Cu and Fe (atomic proportions) in Pt–Fe–Cu alloys from the Pirogues chromitite.

Unnamed Pt–Fe oxides: The compositions of the Pt–Fe oxides from the chromitite mineralization are plotted in Figure 10B. They show a wide Pt–Fe compositional range and Cu enrichment at a constant Pt/Fe ratio. Pd and Rh are the only PGE present in significant amounts in these minerals (ranging, respectively, between 0.2 and 4.2 wt.%, and 0 and 0.5 wt.%). The Cu content reaches 16.8 wt.%, and Ni also is invariably present.

The proportion of Pt–Fe oxide (over alloy) in chromitite varies from one sample to another (Table 2). The composition of the Pt–Fe oxide from the Ni Estuary alluvium is plotted in Figures 7B and 9. In contrast to the alloys, oxides are marked by a Pt/Fe atomic ratio close to unity and a low Rh content. The compositions of Pt–Fe oxides from the Pirogues alluvial suite are plotted in Figure 7A. A wide range of oxygen contents has been recorded, from 1.0 wt.%, which corresponds to the formula $(Pt_{0.97}Fe_{0.81}Pd_{0.01})_{\Sigma1.8}O_{0.2}$, to 10.4 wt.%, corresponding to $(Pt_{0.57}Fe_{0.36}Pd_{0.07})_{\Sigma1.0}O_{1.0}$. The increase in oxygen does not modify the Pt/Fe ratio, which remains, with few exceptions, close to 1. High Pd contents (average 2.9 wt.%, maximum 13.4 wt.%) have been recorded in the oxides (Augé & Legendre 1994).

Tulameenite: Tulameenite was discovered in several of the isoferroplatinum grains from the Pirogues alluvial suite. It occurs as small grains either attached to the host isoferroplatinum, or included in it. The Fe–Cu ratio of the Pt_2FeCu grains is variable (Table 4), one particle having a composition close to the ideal composition (Fig. 7A). No Cu-rich Pt–Fe alloy has been found in the Ni mineralized alluvium. In contrast, a systematic Cu-enrichment is observed in Pt–Fe alloys in the chromitite, with some compositions plotting close to the Pt_2CuFe end-member, which could be interpreted as being tulameenite (Figs. 10A, 11).

Unnamed Pt–Ru–Rh alloy

A mineral with Pt, Ru and Rh as major constituents has been discovered in several grains of isoferroplatinum from the Ni Estuary suite. This phase occurs in two different environments: 1) it forms an apparent matrix of very small rounded grains of Pt_3Fe composition (Figs. 5A, B); this texture suggests a process of high-temperature exsolution, and 2) as "droplets" (2 or 3 μm across, Fig. 4F), or irregular larger crystals apparently trapped in the host isoferroplatinum.

The largest crystals are those that give the lowest Pt and Fe contents, around 53.3–56.9 wt.% and 0.8–2.9 wt.%, and the highest Ru and Rh content (between 21.6 and 27.9 wt.%, and 6.3 and 15.9 wt.%, respectively; see Table 4). The other elements detected in significant amounts include Os (between 0.9 and 5.1 wt.%), Ir (1.0–9.4 wt.%), and Cu (up to 0.6 wt.%). In spite of the small number of analyses considered,

complex elemental substitutions (Os + Ir for Rh + Ru) are observed. Similarly, incorporation of Ru is marked by an increase in Rh. Variations in Pt and Fe are more difficult to evaluate, since they may be due to contamination from the host isoferroplatinum.

The general formula of this phase can be written: $Pt_{0.36–0.44}Ru_{0.26–0.37}Rh_{0.08–0.21}Fe_{0.02–0.1}Ir_{0.01–0.07}Os_{0.01–0.04}$. Taking only the major elements and the lowest Pt content, this can be simplified to $PtRuRh_{0.5}$. This phase is probably a new mineral species. One of its modes of occurrence (Figs. 5A, B) suggests high-temperature exsolution from a complex phase (to give this phase and an isoferroplatinum composition). The proportion of the PtRuRh phase is low, and estimated at 15%. This gives an initial composition that is not very different from an isoferroplatinum composition (with Pt 82.02, Fe 6.77, Cu 0.76, Ir 1.21, Rh 4.36, Ni 0.17 wt.%), but with Os (0.36) and Ru (4.09). The latter two elements, however, have so far not been recorded in significant amounts in isoferroplatinum. This could explain the instability of this phase at a low temperature, resulting in exsolution.

Os–Ir–Ru alloy

Os–Ir–Ru alloy is considered characteristic of podiform chromitite from ophiolites and placers derived from ophiolites. Surprisingly, it has not been found in the Pirogues suite of chromitite, but it should be emphasized that the chromitite samples have very low concentrations of Os, Ir and Ru, lower than mantle chromitite in some cases (Fig. 3). However, lamellae of Os–Ir–Ru alloy have been identified as products of exsolution in isoferroplatinum from the Pirogues alluvium.

Os–Ir–Ru alloy is more common in the Ni Estuary suite, where it occurs either as: 1) discrete grains, 2) two-phase grains with erlichmanite (Fig. 5F), or 3) laths in complex grains of isoferroplatinum. In the third case, the Os–Ir–Ru alloy contains very thin (<1 μm) lamellae of Pt, too thin to be analyzed (Figs. 4F, 5A). Most compositions plot in the osmium field, close to the ruthenium or iridium fields (Harris & Cabri 1991; Table 4, Fig. 12). Individual grains are homogeneous in composition and carry 1.2–15.0 wt.% Pt, which is present in solid solution or as thin laths. Several compositions plot in the miscibility gap defined by Harris & Cabri (1973) and correspond to laths (with up to 15 wt.% Pt in solid solution) adjacent to large grains of osmium.

The analytical data presented here fall in the range of compositions given by Hagen *et al.* (1990) for alluvial alloys derived from an ophiolite. They differ, however, from compositions of osmium in mantle chromitite (Legendre & Augé 1986) in the systematic presence of Pt. Cumulate chromitite from Albania contains inclusions of Os–Ir–Ru alloy with up to 20 wt.% Pt (Neziraj 1992). Peck *et al.* (1992) gave a
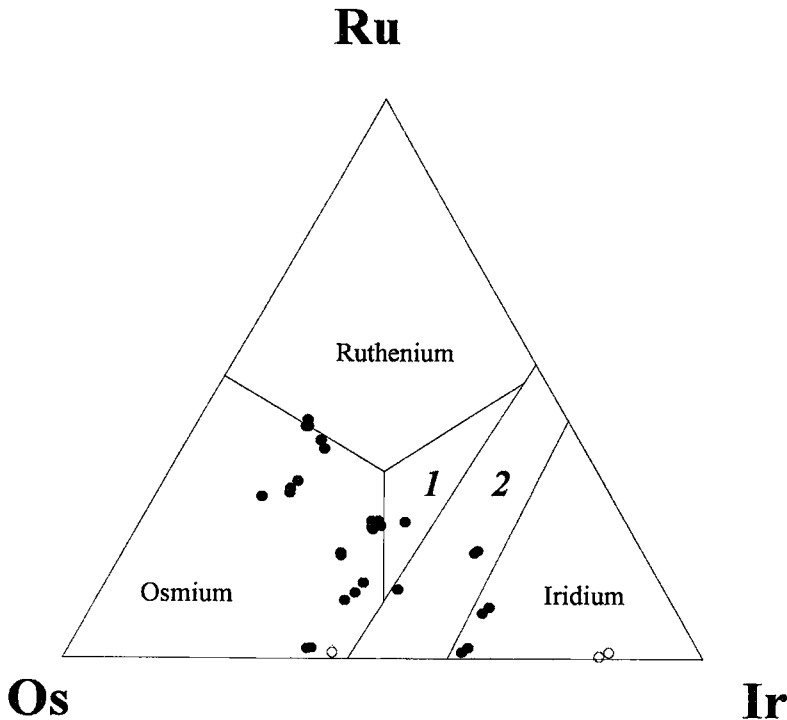
Ru

FIG. 12. Composition of Ir–Os–Ru alloys from mineralized alluvium. Closed circles: Ni, open circles: Pirogues. *1*: field of rutheniridosmine, *2*: miscibility gap.

range of 0 to 2.3 wt.% Pt in grains of alloy from western Tasmania.

Cooperite

Pt sulfides occur almost exclusively in the Pirogues suite of chromitite, where they are irregularly distributed within the mineralized zones (Table 2). They occur as small monophase inclusions in the chromite crystals; in a few cases, small grains of Rh sulfide are adjacent to cooperite (Fig. 4D). Only one 100-μm grain of cooperite has been discovered in the Pirogues alluvium, and one in the Ni Estuary alluvium, where it forms small (10 μm) inclusions in a grain of isoferroplatinum.

The compositions obtained are close to ideal cooperite (Table 5), with low Pd (from 0 to 2.78 wt.%) and Ni contents (from 0.05 to 0.82 wt.%). Rh also was detected in some grains, with a maximum of 1.15 wt.%. The analytical results tend to show an excess of S, with an average formula close to $M_{0.94}S_{1.06}$.

Laurite–erlichmanite series

Two crystals of erlichmanite were discovered, both from the Ni Estuary alluvium (one is associated with iridium as a two-phase grain, the other is included in isoferroplatinum). Laurite is more common; it has been found as inclusions in chromite from the Pirogues suite (where it occurs as isolated crystals or, in rare cases, in a complex association with other PGE sulfides) and in the Ni Estuary alluvium, where it forms large discrete grains or occurs as inclusions in isoferroplatinum or, more rarely, in osmium alloy. Note the absence of laurite from the alluvial suite of the Pirogues zone (Table 3).

The compositions of laurite and erlichmanite are given in Table 5. Laurite from the Pirogues chromitite tends to have a more restricted composition than alluvial laurite from the Ni beach sand, both environments being characterized by a low content of Ir. On the other hand, laurite from the Ni suite is marked by a low but significant enrichment in As (up to 6.3 wt.%), with an As-for-S substitution corresponding to the replacement of one atom of S by one atom of As. A positive linear correlation between Rh and As (Rh reaching 12 wt.%) could indicate the incorporation of RhAsS in the structure of laurite. Other elements entering the laurite are Pt (0–13.1 wt.%), Cu (0–0.4 wt.%) and Ni (0–0.2 wt.%).

Pt, almost systematically detected here, does not occur in Ru–Os sulfide from mantle chromitite. Augé & Legendre (1992) noted that the presence of Pt in

TABLE 5. SELECTED COMPOSITIONS OF PGE SULFIDES

	erlichmanite		laurite				cooperite				bowieite		RhS	
	Ni1	Ni3	Ni4	R1A	Ni6	Ni8	R1B	R1C	R1D	R5A	R1D	Ni9	Ni10	Ni11
	Weight per cent													
Os	64.90	40.95	5.13	11.88	5.77	0.87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ru	1.01	20.64	42.85	41.38	49.96	57.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pt	1.59	0.22	1.06	0.14	4.29	0.41	81.59	79.51	81.91	78.78	0.25	11.84	4.28	4.27
Cr	0.00	0.00	0.00	1.21	0.13	0.12	1.35	2.09	0.86	2.01	2.88	0.00	0.07	0.12
As	0.35	0.00	6.40	0.15	0.74	0.34	0.08	0.01	0.00	0.01	0.00	0.00	0.11	0.06
Ir	5.79	8.21	0.92	1.75	1.33	0.14	0.08	0.03	0.36	0.00	32.01	4.77	1.36	1.36
Pd	0.35	0.00	0.00	0.00	0.28	0.00	1.15	1.10	1.15	1.49	0.00	0.04	0.23	0.63
Co	0.00	0.00	0.03	0.04	0.00	0.03	0.03	0.00	0.03	0.01	0.00	0.00	0.10	0.06
S	25.55	28.72	33.00	35.74	31.45	36.73	15.40	15.45	15.11	15.60	25.96	26.39	20.03	19.97
Fe	0.00	0.05	0.00	1.20	0.45	0.37	0.81	1.46	0.60	1.62	1.88	0.53	1.16	0.93
Rh	0.50	0.66	12.23	6.71	3.93	2.40	0.21	0.35	0.32	0.36	36.72	57.10	71.02	70.42
Cu	0.09	0.08	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.41	0.03	1.06	0.92
Ni	0.05	0.02	0.06	0.04	0.07	0.00	0.10	0.63	0.07	0.48	0.02	0.04	0.84	0.91
Total	100.19	99.55	101.70	100.24	98.40	99.01	100.79	100.62	100.41	100.36	100.13	100.74	100.26	99.65
	Atomic proportions													
Os	28.39	15.74	1.59	3.75	1.91	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ru	0.83	14.93	24.99	24.56	31.04	32.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pt	0.68	0.08	0.32	0.04	1.38	0.12	45.72	44.59	46.21	44.06	0.09	4.10	1.57	1.58
As	0.39	0.00	5.03	0.12	0.62	0.26	0.12	0.01	0.00	0.02	0.00	0.00	0.11	0.06
Ir	2.51	3.12	0.28	0.55	0.43	0.04	0.05	0.02	0.21	0.00	12.42	1.68	0.50	0.51
Pd	0.27	0.00	0.00	0.00	0.16	0.00	1.18	1.13	1.19	1.52	0.00	0.24	0.16	0.42
Co	0.00	0.00	0.03	0.04	0.00	0.03	0.05	0.00	0.06	0.03	0.00	0.00	0.00	0.00
S	66.33	65.48	60.66	66.88	61.60	65.30	52.49	52.71	51.86	53.10	60.39	55.66	44.64	44.82
Fe	0.00	0.07	0.00	0.11	0.37	0.27	0.00	0.00	0.00	0.00	0.00	0.64	1.48	1.20
Rh	0.41	0.47	7.00	3.91	2.40	1.33	0.22	0.37	0.34	0.38	26.60	37.52	49.31	49.24
Cu	0.11	0.09	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.48	0.03	1.19	1.04
Ni	0.08	0.02	0.06	0.04	0.07	0.00	0.18	1.17	0.13	0.89	0.02	0.05	1.03	1.12

Same legend as Table 4.

laurite characterizes minerals derived from a Pt-rich environment. This is confirmed here.

Rh–Ir sulfides

Bowieite: Two grains close to the ideal formula $(Rh,Ir,Pt)_2S_3$ (bowieite) have been discovered. The first (anal. R1D, Table 5), in the Pirogues chromitite, is a thin, 20-μm-long, tabular crystal trapped in chromite, of composition $(Rh_{1.36}Ir_{0.62}Cu_{0.02})_{\Sigma2.0}S_{3.0}$, with minor amounts of Pt (about 0.4 wt.%). The other grain of bowieite was discovered in a complex grain of isoferroplatinum, with small inclusions of laurite, from the Ni Estuary alluvium (anal. Ni9, Table 5, Fig. 5C). This grain, $(Rh_{1.93}Pt_{0.16}Ir_{0.08})_{\Sigma2.17}S_{2.83}$, differs in composition from that discovered in chromitite by its high Pt content and much lower Ir content. It also contains minor Pd (0.1–0.4 wt.%) and Fe (0.1–1.4 wt.%). S is depleted with respect to the ideal formula.

Undetermined Rh sulfide: In the alluvial grain from the Ni Estuary alluvium that contains bowieite, another Rh sulfide (about 20 μm across, Fig. 5C) was analyzed. Its Rh content is high, about 71 wt.%. It also contains Pt (4.4 wt.%), Ir (1.4), Fe (1.0), Cu (1.0), Ni (0.9) and Pd (0.4), and about 20 wt.% S (Table 5). The grain corresponds to $(Rh_{4.44}Pt_{0.14}Fe_{0.13}Cu_{0.11}Ni_{0.09}Ir_{0.05}$

$Pd_{0.01})_{\Sigma4.97}S_{4.02}$, the ideal composition being Rh_5S_4. This gives a metal: sulfide atomic ratio of 1.25, which does not correspond to prassoite ($Rh_{17}S_{15}$ or Rh_3S_4). This phase could be the Rh sulfide equivalent of the compound Pt_5Se_4, described as luberoite by Jedwab *et al.* (1992). Palladseite ($Pd_{17}Se_{15}$), a Pd–Se equivalent of prassoite, has also been described (Davis *et al.* 1977).

Thiospinels

Several PGE sulfides containing Pt, Ir or Rh as PGE and a base metal (Fe, Cu or Ni) were discovered in the Pirogues samples of chromitite. They occur either as discrete crystals or as two-phase grains, associated with cooperite or with base-metal sulfide. Because of their small size and the fact that they are generally associated with other phases, it is difficult to characterize their composition precisely. However, these phases appear clearly to belong to the thiospinel (linnaeite) group, with the general formula $(Fe,Ni,Cu)(Ir,Rh,Pt)_2S_4$ (Table 6). Figure 13A shows two compositional groups: the malanite field (ideally $CuPt_2S_4$), but marked by extensive Pt-for-Rh substitution, and the cuprorhodsite field ($CuRh_2S_4$). Similarly, Figure 13B shows two types of composition, one close to the Cu apex, and the other with a Fe–Cu composition

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TABLE 6. SELECTED COMPOSITIONS OF VARIOUS PGE SPECIES

	thiospinels				hollingworthite		irarsite				sperrylite		stibiopalladinite	
	R5A	R57A	R57B	R57C	Ni1	Ni3	Ni4	Ni5	Ni7	Ni8	Ni9	AP1	Ni1	Ni2
	Weight per cent													
Os	0.00	0.00	0.00	0.00	0.00	0.36	0.41	0.00	1.62	1.28	0.01	0.00	0.00	0.01
Ru	0.00	0.00	0.00	0.59	0.00	0.04	0.84	0.99	4.58	0.00	0.13	0.00	0.00	0.00
Pt	42.48	12.45	2.10	0.52	1.39	1.33	6.46	1.39	0.80	17.25	56.38	57.34	3.46	4.50
Cr	1.16	1.71	2.60	2.35	0.48	0.41	0.00	0.00	0.08	0.00	0.00	0.00	0.15	0.09
As	0.00	0.11	0.09	0.00	31.97	33.23	26.03	26.29	28.28	27.86	41.98	41.48	0.34	3.62
Ir	5.57	24.21	18.92	17.53	0.42	0.19	49.39	40.20	16.66	41.48	0.25	0.10	0.22	0.21
Pd	0.44	0.17	0.00	0.20	0.34	0.44	0.00	0.15	0.00	0.00	0.02	0.00	66.59	68.23
Co	0.21	0.06	0.40	0.26	0.00	0.07	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02
S	26.21	27.82	30.37	30.18	14.43	16.20	11.25	13.95	16.23	7.83	0.55	0.44	0.08	0.07
Fe	1.04	6.67	16.82	12.54	0.87	0.50	0.00	0.00	0.00	0.38	0.09	0.00	0.09	0.93
Rh	16.12	21.84	16.97	20.40	49.29	47.09	4.47	17.17	32.90	0.61	0.81	0.16	0.09	0.00
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	1.03
Cu	9.06	7.69	6.11	9.92	0.06	0.00	0.54	0.40	0.19	0.52	0.00	0.00	1.78	0.09
Sb	0.00	0.00	0.00	0.00	0.96	0.19	0.00	0.10	0.00	0.00	0.00	0.00	28.88	21.13
Ni	0.18	0.57	7.91	5.18	0.07	0.01	0.02	0.00	0.02	0.05	0.00	0.00	0.04	0.01
Total	102.47	103.30	102.29	99.67	100.30	100.14	99.43	100.63	101.41	97.41	100.22	99.52	102.07	99.94
	Atomic proportions													
Os	0.00	0.00	0.00	0.00	0.00	0.13	0.21	0.00	0.63	0.71	0.01	0.00	0.00	0.01
Ru	0.00	0.00	0.00	0.35	0.00	0.03	0.79	0.83	3.36	0.00	0.15	0.00	0.00	0.00
Pt	15.85	4.27	0.62	0.16	0.51	0.48	3.15	0.60	0.30	9.32	32.89	34.05	1.91	2.51
As	0.00	0.10	0.07	0.00	30.61	30.99	33.05	29.56	27.93	39.19	63.77	64.14	0.49	5.26
Ir	2.11	8.42	5.72	5.44	0.16	0.07	24.44	17.62	6.42	22.74	0.15	0.06	0.13	0.12
Pd	0.30	0.11	0.00	0.11	0.23	0.29	0.00	0.12	0.00	0.00	0.02	0.00	67.68	69.98
Co	0.26	0.07	0.40	0.26	0.00	0.17	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
S	59.49	57.99	55.10	56.16	32.28	35.13	33.38	36.64	37.44	25.74	1.93	1.57	0.27	0.25
Fe	0.00	6.13	15.06	11.12	1.12	0.63	0.00	0.00	0.00	0.72	0.17	0.00	0.18	1.82
Rh	11.40	14.18	11.83	11.83	34.37	31.97	4.13	14.05	23.66	0.62	0.89	0.18	0.09	0.00
Cu	10.37	8.09	5.59	9.31	0.07	0.00	0.81	0.52	0.22	0.86	0.00	0.00	3.02	0.15
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.88
Sb	0.00	0.00	0.00	0.00	0.57	0.11	0.00	0.07	0.00	0.00	0.00	0.00	25.81	19.01
Ni	0.22	0.65	7.84	5.27	0.08	0.01	0.04	0.00	0.03	0.09	0.00	0.00	0.07	0.02

Same legend as Table 4.

(with a slight enrichment in Ni). The former corresponds exactly to the malanite composition, whereas the latter corresponds to the minerals plotted in the cuprorhodsite field, which are enriched in Fe. A similar observation was made by Johan *et al.* (1990) for cuprorhodsite from the Durance River alluvium.

Ir and Rh sulfarsenides

Irarsite (IrAsS) and hollingworthite (RhAsS) have been identified in the Ni alluvial samples only. They occur as small crystals adjacent to isoferroplatinum or included in it. One grain is a complex association of hollingworthite, irarsite and sperrylite. Irarsite and hollingworthite present a large compositional range. Other elements detected in significant amounts include Os (up to 4.76 wt.%), Ru (up to 7.2), Pd (up to 0.44), Fe (0.96) and Cu (0.54, see Table 6).

Sperrylite

Sperrylite is present as discrete grains in the Pirogues mineralized alluvium and in a complex irarsite–hollingworthite grain in the Ni Estuary. The sperrylite grains are close to the ideal $PtAs_2$ composi-

tion (Table 6). Os (up to 0.3 wt.%), Ru (0.2), Pd (0.2) and Rh (1.2) have been detected sporadically, whereas Ir (up to 0.8) is systematically present. Fe (up to 0.7 wt.%) also was detected in most grains, as was S (0.2 to 0.7 wt.%).

Stibiopalladinite

Stibiopalladinite (ideally Pd_5Sb_2) occurs in two grains of isoferroplatinum of the Ni alluvium as small crystals at the boundary between irarsite and isoferroplatinum. The compositions obtained (Table 6) are similar: $(Pd_{4.76}Cu_{0.21}Pt_{0.13}Ir_{0.01})_{\Sigma 5.11}(Sb_{1.81}As_{0.03}Te_{0.02} S_{0.02})_{\Sigma 1.89}$. The Cu content seems to be particularly high.

DISCUSSION

Two types of chromitite have been identified in the New Caledonia ophiolite complex, with which two types of PGE enrichment are associated: mantle-derived chromite deposits (such as Tiébaghi) with a long history of exploitation, containing Os–Ir–Ru in the form of alloy and sulfides, and chromite concentrations in the cumulate series, containing the Pt
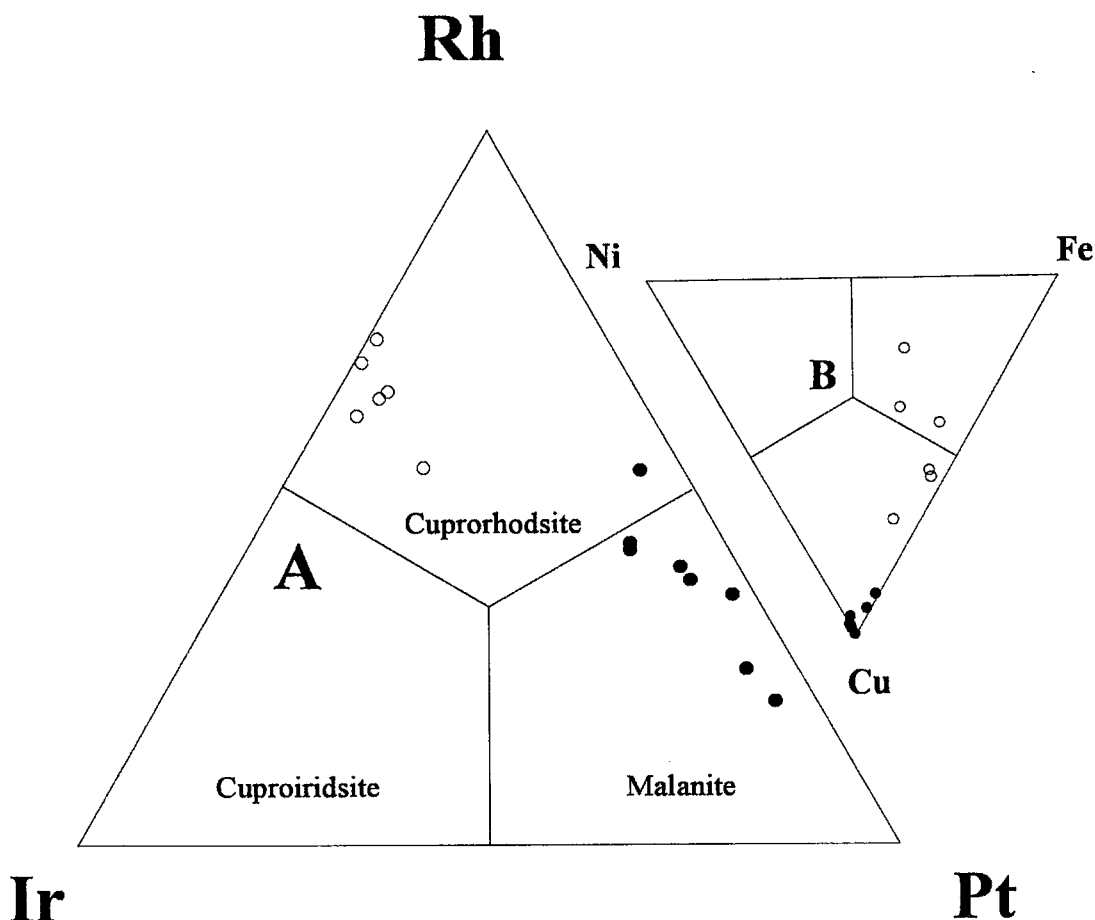
FIG. 13. Composition of PGE thiospinels from the chromitite mineralization A) in terms of the triangular diagram Rh–Ir–Pt (closed symbols correspond to Cu-rich minerals), and B) in terms of the triangular diagram Cu–Fe–Ni (closed symbols correspond to Pt-rich minerals).

enrichment described here.

The two types of chromitite – PGE mineralization show similarities, such as in the mode of the occurrence of the PGM, systematically as inclusions in chromite crystals, and the coexistence of PGE alloy and sulfides. On the other hand, the two types are distinguished by the nature of the PGM, their size and abundance, and the texture and composition of the host chromitite, suggesting major differences in the environment in which they crystallized.

Host chromitite

Typical textures of mantle chromitite indicate crystallization in a turbulent milieu (Lago *et al.* 1982), whereas the textures of stratiform chromitite suggest crystallization in quieter conditions. Mantle chromitite

is characterized by Cr-rich, Fe^{3+}-poor chromite, typical of podiform chromite, crystallizing from a primitive melt at low oxygen fugacity. Stratiform chromitite and chromitite in dykes, marked by a relatively low content of Cr and strong Fe^{3+} and Ti enrichment, have crystallized from a more evolved (Al–Ti-enriched, Cr–Mg-depleted) melt under more oxidizing conditions. The presence of interstitial silicates, olivine in mantle chromitite and pyroxene in cumulate ore, points in the same direction.

Origin of the PGE enrichment

The origin of PGM in mantle chromitite has been ascribed to the early crystallization of small Os–Ir–Ru PGM in a conduit (according to the model of Lago *et al.* 1982), the PGM then being trapped, acting as

nuclei, during chromite formation (Augé 1985). The absence of PGM in the surrounding silicates and of sulfide phases related to the PGE mineralization leads us to suggest the same mechanism for the Pirogues chromitite, *i.e.*, the crystallization of chromite in an environment that already contained the PGM, the chromite trapping the PGM.

The abundance of PGM in a thin layer (represented by the chromite layer) suggests that the mineralization resulted from the sudden nucleation of the PGM at a certain level of the magma chamber. Crystallization of chromite could have been induced by the presence of the PGM in the magma, which facilitates nucleation because of the property of the PGM of reducing the activation energy for crystallization (Capobianco & Drake 1990).

A complex assemblage of PGM is present in the Pirogues chromitite (Table 3). In terms of conditions of crystallization, the coexistence of PGE alloy and sulfide is difficult to interpret, as this would require a large range of temperature and $f(S_2)$, incompatible with their presence in a single sample. A possible explanation is that the different species are not in thermodynamic equilibrium. The milieu from which the PGM have crystallized evolved rapidly in a closed system [with local increase in $f(S_2)$ due to chromite crystallization]; the entrapment of the early PGM in chromite did preclude any subsequent re-equilibration, thus preserving a complex assemblage of minerals. The presence of base-metal sulfides (BMS) in chromitite, probably due to oversaturation in sulfur, illustrates the incompatibility. We consider that the assemblage included in chromite is a high-temperature one, PGM having crystallized above 1050°C (temperature estimated using pyroxene geothermometry in chromitite).

Clearly, the platinum mineralization and the crystallization of chromite are genetically linked; the concentration factor (in a hypothetical magma) for both Pt and Cr is of the same order of magnitude. On the basis of a simplified figure of 30 ppb Pt in the magma and 3 ppm in the ore, and 0.4% Cr_2O_3 in the magma and 40% in the chromite horizons, the concentration factor can be estimated to be 100. It is thus not necessary to envisage two different processes for concentration of chromite and PGE. Both Cr and PGE could have been collected from a volume of magma several hundred times that of the ore.

The effect of oxygen fugacity on the solubility of PGE is important, as shown experimentally by Amossé *et al.* (1990) and Amossé & Allibert (1993). An increase in oxygen fugacity results in a decrease in Ir solubility, whereas the solubility of Pt also decreases but remains higher than that of Ir. This could explain the observation made here, of crystallization of Ir (associated with Os and Ru) as an alloy in mantle chromitite at low oxygen fugacity, and crystallization of Pt alloy at a higher oxygen fugacity, higher in the ophiolite sequence, *i.e.*, in the cumulate series

(Fig. 14). This hypothesis has been proposed by Amossé *et al.* (1990) to explain the presence of Pt–Fe alloy included in chromite crystals in Alaskan-type complexes. Roeder & Jamieson (1992) have determined experimentally the composition of chromite and coexisting Pt–Fe alloy under magmatic conditions. They showed that a decrease in $f(O_2)$, increasing the activity of Fe in the alloy relative to that of the oxidized iron species, could stabilize the alloy.

Other authors have investigated the partitioning of PGE between spinel and silicate melt. Capobianco & Drake (1990) concluded that Ru and Rh are strongly compatible in spinel, whereas Pd is strongly incompatible. However, the role of PGE partitioning into the spinel structure on the formation of PGE concentrations has not been clarified. Similarly, the hypothesis that PGM are formed by exsolution from the host chromite has been rejected (Augé 1988), and there is no reason to reconsider this possibility.

The distribution of the PGE-chromite-enriched zones associated with dykes suggests that the crystallization of the PGM and the associated chromite results in complex and suddenly occurring processes. Seams of chromite and concentrations of chromite in cumulates and dykes enriched in orthopyroxene in an ophiolite are uncommon and require special conditions. We suggest that crystallization of chromite (and of the included PGM) results from influx of a mafic, Cr-rich magma into the chamber, with interaction of the two liquids. The abundance of dykes in the Pirogues area and the discontinuity of the mineralized zones at a meter scale argue for numerous injections of magma at the base of the chamber. The initiation of mixing between the new magma and its host will promote changes in the physical conditions [increase in $f(O_2)$, decrease in T]. These new conditions, together with low fugacity of S in the magma, will promote sudden crystallization of the PGE (Amossé *et al.* 1990), which will be accompanied or followed by precipitation of chromite (due to the same variations in the physical conditions, see Irvine 1981). The close association of the two suggests that this process occurs in a restricted zone, at the interface between the two magmas, represented by the mineralized layer. A similar mechanism has recently been proposed by Pedersen *et al.* (1993) to explain Pt mineralization in ophiolitic cumulates of the Leka ophiolite, Norway. The nature of the rocks mineralized in PGE (*i.e.*, abundance of orthopyroxene, presence of chromite concentrations crystallized from an evolved liquid) suggests that they could have been derived from a Cr–Mg–Si-rich magma, of possible boninitic affinity.

PGM in chromitite versus placer and laterite

The differences between primary and alluvial mineralization in the Pirogues suite are readily interpreted in terms of weathering and different methods of
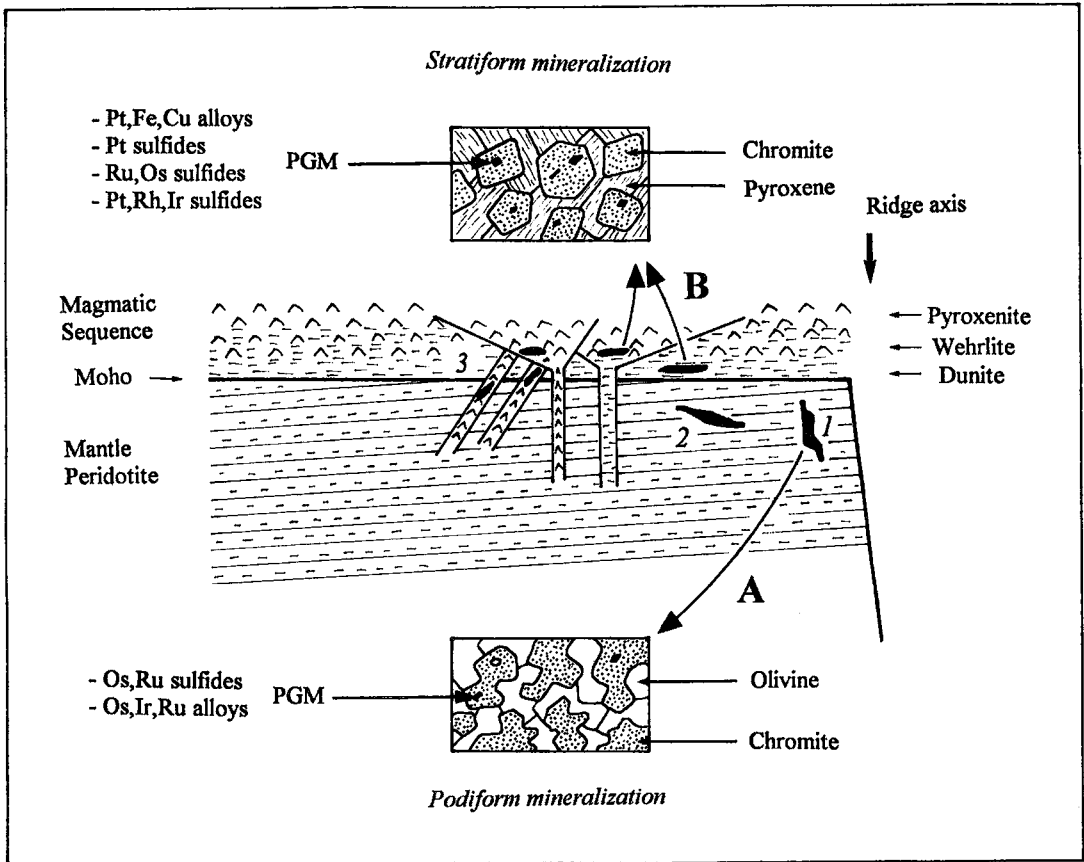
FIG. 14. Location and characteristics of "podiform" (A) and "stratiform" (B) chromitite – PGE deposits in the New Caledonia ophiolite. 1. Emplacement of podiform chromitite at the ridge axis. 2. Deformation of the podiform bodies due to mantle flow. 3. Emplacement of the chambers and dykes where PGM and stratiform chromitite crystallize.

sampling. PGE sulfides (cooperite, laurite and thiospinels), representing more than 50% of the PGM grains in chromitite, are lacking in the alluvial mineralization. This could be explained by a sampling bias, since the PGE sulfides in chromite, in contrast to the Pt–Fe alloys, form very small grains, which cannot be recovered in the heavy-mineral concentrates. However, the reduced presence of Os–Ir–Ru alloy, a mineral classically described in placers deriving from ophiolites (Cabri & Harris 1975, Hagen et al. 1990) and recognized in the mantle chromitite of the Massif du Sud (Table 3), must be emphasized.

Many PGM from the alluvial suite show textures attributed to solution during surface weathering; "near-perfect crystal form", such as those described from alluvial nuggets (interpreted by some authors as the result of mineral growth in the surface environment: see Bowles 1986) are very rare.

The Ni alluvial suite differs significantly from the Pirogues suite (Table 3) in the nature and diversity of PGM. Pt–Fe alloys are the most common minerals, but represent only 40% of the grains, followed by Os–Ir–Ru alloy (10%), laurite (10%), and hollingworthite (10%). The location of the mineralization (beach sand at the Ni Estuary) gives no indication of its origin. However, the zone as a whole corresponds to a typical harzburgitic mantle series. Sequences of cumulate appear 20 km farther south (in a zone that is not drained by the Ni River). The mineralization must have originated in another type of unit, probably part of the mantle series. It should be noted that alluvial Pt–Fe minerals were also found in the Tiébaghi massif, where cumulate rocks are totally absent (Augé 1993). A preliminary survey indicates the possibility that pyroxenite dykes are a possible source of the grains. Similar dykes, which are very abundant in the Ni region, could be the source of the mineralized alluvium.

Comparison with other environments

Among the ophiolite complexes where significant Pt enrichment has been described, two show strong analogies with the Pirogues suite; these are the Estrie-Beauce ophiolite in Quebec (Gauthier *et al.* 1990) and the Tropoja ophiolite in Albania (Ohnenstetter *et al.* 1991). Another, the Leka ophiolite complex in Norway, shows differences that deserve to be stressed.

Pedersen *et al.* (1993) described PGE-enriched rocks in the Leka complex. They identified Pt and Pd enrichment in mantle chromitite, which appears in some ways similar to some of the Unst chromitite (Prichard & Tarkian 1988). In contrast to the observations made here, the stratiform chromitite in the Leka ophiolite is depleted in Pt (and Pd). Such depletion is explained by the fact that the Pt (and Pd) concentrations are displaced relative to chromite: Pt enrichment is observed above the chromitite, and Pd enrichment is observed in sulfide-rich horizons. Pedersen *et al.* (1993) suggested that the PGE were scavenged from the parental magma shortly after it entered the magma chamber, and before it mixed with the resident magma. The lack of Pd mineralization in New Caledonia is easily explained by the lack of sulfides, which are known to collect Pd. The main difference between the Leka and New Caledonia ophiolites is that PGM crystallization was not accompanied by chromite crystallization in the Leka ophiolite. This difference shows that the presence of chromite is not necessary to preserve the PGE mineralization. However, the Pt content recorded in the New Caledonia samples is much higher than that observed the stratiform Pt mineralization in the Leka ophiolite. This indicates that chromite is an efficient PGE "collector". Attention should be focussed on and above the chromitite in the context of prospection for "stratiform Pt deposits" in ophiolite.

The ophiolitic mineralization of the Pirogues River also shows striking similarities to Alaskan-type mineralization. Samples of chromitite at Tulameen, British Columbia, are strongly enriched in Pt with respect to the other PGE. Their composition, marked by Ti and Fe^{3+} enrichment, is very similar to the chromitite described here, and the primary high-temperature PGM paragenesis is composed of a complex Pt–Fe–Cu alloy, laurite and erlichmanite (Nixon *et al.* 1990), the concentration of PGE in chromitite being interpreted as taking place by the accumulation of PGM directly segregated from the magma.

Johan *et al.* (1989) described PGE mineralization mainly composed of Pt–Fe alloys, cooperite, erlich-manite, sperrylite, malanite and Pt–Pd antimonides in clinopyroxenite of an Alaskan-type complex. Similarly, nuggets derived from Alaskan-type complexes (Nixon *et al.* 1990, Johan *et al.* 1991, Slansky *et al.* 1991) are very similar in terms of

paragenesis to the mineralized alluvium described here. However, an important difference lies in the presence of silicate and glass inclusions in Pt–Fe nuggets from Alaskan-type complexes (Nixon *et al.* 1990, Johan *et al.* 1991, Augé & Legendre 1992), the nature of which suggest a high partial pressure of H_2O in the melt. Such inclusions were not found here. However, we wish to emphasize that a mineralogical study of the Pirogues and Ni mineralized alluvium alone would certainly not have suggested an ophiolitic source, but rather an "Alaskan-type intrusion that has yet to be identified".

Certain samples of stratiform chromitite show very high enrichment in PGE, *e.g.*, the chromitite in the Middle and Upper groups of the Bushveld complex and the A chromitite of the Stillwater complex. Lee & Parry (1988) and Teigler (1990) have shown that PGE concentration increases with stratigraphic height, and Von Gruenewaldt *et al.* (1986) emphasized the differences in the PGE distribution between the various layers of chromite in the Bushveld complex and the Merensky reef. They found that the PGE mineralization occurs as sulfides (laurite) and arsenide included in chromite crystals, but in many cases Pt and Pd minerals are in close association with base-metal sulfides, interstitial to the chromite.

Thus, in contrast to ophiolitic or Alaskan-type mineralization, base-metal sulfides have played a major role in PGE mineralization associated with chromite layers in stratiform complexes. Naldrett & Von Gruenewaldt (1989) suggested that in a first stage, the PGE in the chromite-rich layers were collected by a sulfide liquid. In a second stage, desulfurization leaves PGE-rich chromitite containing very sparse sulfides. Such a process cannot be invoked for mineralization in an ophiolitic setting.

CONCLUSIONS

(1) The New Caledonia ophiolite contains two types of chromite deposits (podiform deposits in the mantle sequence, and stratiform deposits in the cumulate sequence) with which two types of PGE mineralization are associated: a typical Os–Ru–Ir association in the podiform chromitite, and a Pt-dominant association in the stratiform chromitite. In both cases, the PGE enrichment is due to the presence of PGM trapped in chromite after crystallization from the melt.
(2) The constant association of chromite and PGM (dominated by Pt minerals) in chromite of the Pirogues cumulates suggests that PGM induced chromite nucleation. Thus chromite crystallization plays a major role in trapping and preserving the PGE mineralization.
(3) The levels enriched in chromite and PGE correspond to influxes of new magma into the chamber. PGM crystallization is promoted by the new conditions in which the melt finds itself, and is facilitated by the low fugacity of S prevailing in the magma. A possible

explanation for the complex PGM paragenesis described in the Pirogues suite (with isoferroplatinum, tulameenite, and undetermined Pt–Fe–Cu alloys, cooperite, Os–Ir–Ru alloy, laurite, bowieite, malanite, cuprorhodsite, sperrylite, and BMS with PGE in solid solution) is that they were formed under thermodynamic disequilibrium because the environment evolved rapidly in a closed system, with local changes in $f(O_2)$, $f(S_2)$ and proportion of PGE, without possible re-equilibration after entrapment in the chromite.

(4) The Pirogues River Pt-enriched suite shows several analogies with Alaskan-type PGE-enrichment, but differs significantly in mode of Pt mineralization from chromitite layers in stratiform complexes. A sulfide phase has probably played a major role in the PGE concentration in the latter, but this is not the case in ophiolite and Alaskan-type suites.

(5) The study of mineralized alluvium derived from primary mineralization has revealed solution features affecting certain grains, confirming a certain mobility of the PGE during lateritic weathering. This has led to the formation of PGE oxides in lateritic soils.

(6) In the Ni mineralized alluvium, a complex paragenesis of the PGM includes isoferroplatinum, an unnamed Pt–Ru–Rh alloy, cooperite, Os–Ir–Ru alloy, laurite, erlichmanite, bowieite, irarsite, hollingworthite, sperrylite, stibiopalladinite and unnamed PGE oxide and Rh sulfide. This association was derived from a source (not identified) that differs from that of the Pirogues suite, since cumulates are absent in this zone.

(7) The presence of a wide spectrum of PGM, therefore, suggests that ophiolitic PGE mineralization need not be confined to a limited group of PGM, and indicates that ophiolites should be reinterpreted for their potential in PGE enrichment.

ACKNOWLEDGEMENTS

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