# PLACER Os-Ir-Ru ALLOYS AND SULFIDES: INDICATORS OF SULFUR FUGACITY IN AN OPHIOLITE?

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#### Abstract

Two types of placer assemblages of platinum-group minerals are recognized from ophiolite settings. One is exclusively composed of grains of Os–Ir–Ru alloy, and occurs in Hokkaido, Japan. The alloys consist of Ru-poor and Ir-rich osmium, iridium (up to 11 at.% Ru), rutheniridosmine, and ruthenium (up to 92 at.% Ru). The other type comprises osmium and iridium with lower Ru content, and primary laurite with significant amounts of Os and Ir. Samar, in the Philippines, is the typical locality. The difference in the assemblages is attributed to the prevailing condition of sulfur fugacity at the initial stage of their crystallization in the upper mantle.

Keywords: platinum-group minerals, Os-Ir-Ru alloys, laurite, placer, sulfur fugacity, ophiolite, mantle, Hokkaido, Japan, Samar, Philippines.

# Sommaire

On trouve deux types d'assemblages de minéraux du groupe du platine en alluvions dans les milieux ophiolitiques. Dans le premier type, il s'agit uniquement de grains d'alliages à Os-Ir-Ru; c'est ce que nous trouvons à Hokkaido, au Japon. Dans ce groupe se trouvent: osmium pauvre en Ru et riche en Ir, iridium (jusqu'à 11% Ru, proportion atomique), rutheniridosmine, et ruthénium (atteignant 92% Ru). L'autre type comprend osmium et iridium à faible teneur en Ru, et laurite primaire contenant des quantités importantes d'osmium et d'iridium. Samar, aux Philippines, en est une localité typique. La différence dans ces assemblages serait due à la fugacité du soufre au stade initial de cristallisation, dans le manteau supérieur.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, alliages à Os-Ir-Ru, laurite, alluvions, fugacité du soufre, ophiolite, manteau, Hokkaido, Japon, Samar, Philippines.

## INTRODUCTION

Refractory Os–Ir–Ru alloys are regarded as the typical platinum-group minerals (PGM) commonly associated with mantle-derived ophiolitic ultramafic rocks (Contstantinides *et al.* 1980, Augé 1985, Prichard *et al.* 1986, Tarkian 1987, McElduff & Stumpfl 1990). Recently, Harris & Cabri (1991) compiled compositional data for more than four hundred samples of PGM alloy from worldwide localities, and presented them on an Os–Ir–Ru diagram, together with their revised nomenclature (Fig. 1). The data plot in two groups: one along the Os–Ir join, and the other along the Os<sub>50</sub>Ir<sub>50</sub>–Ru line. In an earlier compilation of compositions

in the system Os–Ir–Ru (Harris & Cabri 1973), the alloys from Papua New Guinea were shown to have a wide compositional range. In contrast, eleven samples of alloy out of twelve from southeastern Kalimantan (Borneo) are poor in Ru (less than 5 wt%; Stumpfl & Tarkian 1973) and, therefore, plot along the Ir–Os join. Although compositional data on PGM alloys have been accumulating (*cf.* Cabri *et al.* 1996), the regional variation in their Ru contents has not been well explained.

The rarity of PGM hosted by ophiolitic ultramafic rocks does not allow a detailed and comprehensive assessment of their mode of formation and the condition of the melt from which they crystallized. In practice, most of our knowledge on ophiolite-related PGM

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FIG. 1. Os-Ir-Ru diagram showing the composition of alloy in this system from worldwide occurrences. Data from Papua New Guinea (Harris & Cabri 1973), southeastern Borneo (Stumpfl & Tarkian 1973), and the compilation of Harris & Cabri (1991). The nomenclature (IR: iridium, OS: osmium, RU: ruthenium, RIO: rutheniridosmine) and miscibility gap (shaded) are those of Harris & Cabri (1991).

has been obtained from studies of associated placer concentrates. However, this approach has disadvantages, because the uncertainty of their origin usually puts a constraint on the scope of the investigation. A very thorough and systematic investigation of placer PGM collected proximal to the ultramafic bodies is considered to be invaluable. Placer PGM originating from relatively recently emplaced ophiolites in Hokkaido, Japan, and eastern Samar, Philippines, were studied for this purpose.

In this paper, we present a brief description of the geology and PGM mineralogy in these areas, and discuss the role of sulfur in the very early stage of crystallization in the ophiolite.

# GEOLOGICAL SETTING

The islands of Hokkaido and Samar are located in the western part of the Circum-Pacific archipelago (Fig. 2). Both constitute an arc-type association, and have in common a tectonically disrupted ophiolite sequence in the arc system.

# Hokkaido

The north-south-trending Kamuikotan ophiolitic complex (Komatsu *et al.* 1977) in central Hokkaido consists of ultramafic rocks, both high- and low-pressure metamorphic rock-types, and Mesozoic volcanic and sedimentary rocks. In the complex, serpentinite *mélange* (*e.g.*, Mt. Yubari-dake area; Nakagawa & Toda 1987) and dismembered ophiolite (*e.g.*, Horokanai area; Asahina & Komatsu 1979) are observed locally. Although the ultramafic rocks have been largely altered to serpentinite, pseudomorphs and relict minerals show they were mostly dunite and harzburgite that had formed part of a strongly depleted ophiolite (Katoh & Nakagawa 1986).



FIG. 2. Map of PGE and Au placers and serpentinite in Hokkaido, Japan, showing localities of placer PGM for this study. Modified from Watanabe *et al.* (1986) and Yanaga (1984). T: Teshiogawa River, U: Uryugawa River, I: Ishikarigawa River, Y: Yubarigawa River, S: Sorachigawa River.

The complex is well known for numerous placer deposits of PGM in and around the lenticular bodies of serpentinite (Fig. 2; Suzuki 1952, Urashima *et al.* 1974); however, serpentinite-hosted PGM had not been detected prior to the study of Nakagawa *et al.* (1991). Placer PGM samples were obtained from alluvial stream sediments near (less than 10 km) the ultramafic bodies in two representative localities: the western foot of Mt. Yubari-dake and the Horokanai placer chromite mine (Fig. 2). The samples from the Mt. Yubari-dake were collected by local amateur collectors with traditional skills, and those from the mine comprise a part of the Bamba collection of the Geological Survey of Japan (GSJ), Hokkaido Branch.

Part of both ultramafic bodies exhibit a wellpreserved layering of dunite and harzburgite. Both high- and low-pressure-type metamorphic blocks are included in the serpentinite matrix of the Mt. Yubari-dake body (Nakagawa & Toda 1987). On the other hand, numerous dikes of diorite are found within the serpentinite body near the Horokanai mine (Igarashi *et al.* 1985). Lithological characteristics of these ultramafic bodies are the absence of clinopyroxene-bearing lithofacies and podiform-type chromite deposits, and the occurrence of accessory chromite with high Cr/(Al + Cr).

# Eastern Samar

Prior to the discovery of platinum-group elements (PGE) mineralization in an ophiolitic complex by Constantinides et al. (1980), the occurrence of PGE was already known at the Acoje chromite mine in the Zambales mountain range on the western coast of Luzon Island, Philippines (Hulin 1950). The Acoje mine produced commercial quantities of PGE as a by-product over the period 1970-1975, and is the only known PGE producer in the Philippines (BMG 1986). Previous studies concerning PGE in the Philippine archipelago have focussed exclusively on the Acoje mine (Bacuta et al. 1988, 1990, Orberger et al. 1988, 1990). In addition to the Zambales ophiolite, eight other ophiolite belts are recognized in the archipelago (BMG 1986), and host some of the major deposits of chromite in the country. A majority of these chromite deposits are of the high-chromium type (Balce et al. 1981), and are thus also expected to become good PGE producers (Yumul 1993).

Recently, an occurrence of placer platinum-group minerals (PGM) was found in laterite on Samar and Dinagat islands (Franco *et al.* 1993), where an ophiolite sequence is situated. The ophiolite complex is part of the Eastern Bicol – Eastern Mindanao ophiolite belt on



FIG. 3. Simplified geological map and sampling localities of eastern Samar, Philippines. Modified from Franco *et al.* (1993). D: Dinagat Island, EB: Eastern Bicol, SS: Samar–Surigao, PP: Pujade Peninsula, B: Bigan River.

the Pacific coast of the archipelago (Fig. 3). Mining and prospecting for chromite have been active in the ophiolite belt (UNDP: Louca & Makela 1995, JICA & MMAJ 1990). Although these islands are well known for placer gold, none of the small-scale miners paid attention to the PGM associated with the gold and chromite.

The Eastern Bicol – Eastern Mindanao ophiolite belt runs from the eastern part of Bicol Peninsula to Eastern Mindanao through Samar Island and Dinagat Island group (Fig. 3). This belt constitutes a complete but tectonically disrupted ophiolite sequence bounded on the east by the Philippine Trench; the belt is composed of three segments, namely, Eastern Bicol, Samar–Surigao and Pujade Peninsula. Samar Island occupies the northern portion of the Samar–Surigao ophiolite segment, and hosts several productive deposits of chromite (BMG 1981, 1986).

The Late Cretaceous ophiolite block in Eastern Samar outcrops on the southeastern part of the island (Garcia & Mercado 1981). It is composed predominantly of harzburgite tectonite and cumulate dunite with minor dunite-hosted massive to disseminated chromitite, layered gabbro and altered basalt. These ultramafic facies underwent pervasive serpentinization. The ophiolite block is characterized by a series of northwest-trending thrust slices that generally dip to the east, constituting a repetitive sequence of the ophiolite suite. The oldest overlying non-ophiolitic formation consists of volcanic and pyroclastic rocks with sandstone, mudstone, and limestone interbeds dated as Late Oligocene (BMG 1981). The catchment area is drained by minor tributaries of the Llorente and Bigan rivers, and grains of PGM were panned together with placer gold and chromite from an eluvial laterite capping the ultramafic suite.

# MINERALOGY OF OS-Ir-Ru ALLOYS AND SULFIDES

The PGM grains mounted in an epoxy resin were polished for optical observation and coated with a thin layer of carbon for electron-microprobe analysis using the Shimadzu EPMA-8705 instrument at the Geological Survey of Japan, Hokkaido Branch. An accelerating voltage of 20 kV was used with a 10-nA beam current on an MgO standard. Pure metals were employed as standards for all elements, except S, for which pyrite was used. The concentration of ten elements was established using the following X-ray lines: PtL $\alpha$ , IrL $\alpha$ , OsM $\alpha$ , PdL $\alpha$ , RuL $\alpha$ , CuK $\alpha$ , NiK $\alpha$ , CoK $\alpha$ , FeK $\alpha$ , and SK $\alpha$ . The X-ray intensities were treated using ZAF corrections. Representative analytical results are presented in Table 1.

## Hokkaido

More than 60 PGM grains were examined from each locality (Table 2). They range in size from 0.2 to 1.3 mm.

Locality	Horokanai (Hokkaido)			Yubari-dake (Hokkaido)			Samar (Philippines)			
Sp. No.	H52	H87a	H88	Y18	¥82	¥88	AW11	AB45	RB51	AB42
weight %	Os-Ir-Ru alloys						Laurite			
Os	44.82	26.14	7.71	90.74	43.16	26.66	19.31	55.45	25.53	21.54
Ir	45.43	65.22	6.20	6.92	43.82	71.61	73.07	33.13	6.95	3.88
Ru	8.24	4.46	78.75	1.94	12.69	1.43	0.74	7.31	36.13	42.64
Rh	0.26	0.33	2.05	0.09	0.43	0.60	-	-	0.63	0.65
Pt	0.70	3.52	4.58	-	-	-	6.29	3.05	-	-
Pd	-	0.07	-	-	-	-	0.16	0.31	-	-
Fe	0.12	0.42	0.17	0.10	0.23	0.37	0.36	0.12	-	-
Ni	-	-	0.12	0.12	0.15	0.19	-	-	-	-
Cu	-	-	0.10	-	0.12	0.10	-	-	-	-
S	-	-	-	-	-	-	-	-	30.94	31.85
TOTAL	99.57	100.16	99.68	99.91	100.60	100.96	99.93	99.37	100.18	100.56
atomic proportion										
Os	0.419	0.250	0.045	0.888	0.383	0.257	0.192	0.523	0.082	0.067
Ir	0.421	0.616	0.036	0.067	0.384	0.685	0.718	0.310	0.022	0.012
Ru	0.145	0.080	0.864	0.036	0.212	0.026	0.014	0.130	0.217	0.247
Rh	0.005	0.006	0.022	0.002	0.007	0.011	-	-	0.004	0.004
Pt	0.006	0.033	0.026	-	-	-	0.061	0.028	-	-
Pd	-	0.001	-	-	-	-	0.003	0.005	-	-
Fe	0.004	0.014	0.003	0.003	0.007	0.012	0.012	0.004	-	-
Ni	-	-	0.002	0.004	0.004	0.006	-	-	-	-
Cu	-	-	0.002	-	0.003	0.003	-	-	-	-
S	-	-	-	-	-	-	-	-	0.675	0.670

 TABLE 1. REPRESENTATIVE CHEMICAL CONPOSITION ANALYSES OF PGM FROM

 HOKKAIDO AND SAMAR

-: below detection limit

The grains from both localities consist mainly of Os-Ir-Ru alloy. All the grains from Mt. Yubari-dake consist of homogeneous Os-Ir-Ru alloy showing a euhedral to subhedral shape (Fig. 4A); no S- or As-containing phase was observed. This appears to be a common characteristic of PGM grains from the southern part of the complex, such as in Mukawa (Ohta & Nakagawa 1990). On the other hand, about one-half of the PGM grains from Horokanai show similar mineralogical affinities (Fig. 4B) to those from Mt. Yubari-dake, but the crystals are partly replaced by microtextural intergrowths of PGE sulfide, antimonide or arsenide (Figs. 4C, D). Although the chemical compositions of the grains of Os-Ir-Ru alloy from both localities occupy a similar field in the Os-Ir-Ru diagram (Fig. 5), the bulk of the material from Horokanai plots closer to the rutheniridosmine - iridium miscibility gap.

Most of the replacement of individual alloy grains occurs at margins and along cracks. This suggests that laurite ( $RuS_2$ ), as well as the arsenides and antimonides found along cracks and rims of grains of Ir–Os–Ru alloy from Horokanai area, are products of alteration similar to the ones described by Stumpfl & Tarkian (1976). As there are an extraordinary number of diorite

TABLE 2	NUMBER	OF DISCRETE	PGM	GRAINS	INVESTIGATED
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Locality	Hok	Eastern Saman	
discrete grains	Horokanai	Yubari-dake	
Os-Ir-Ru alloy	34	59	28
altered Os-Ir-Ru allov*	27	-	1
laurite	(24)*	-	27(1)*
Pt-Fe (-Pd-Cu) alloy	(2)**	2(13)**	72(2)**
Pt sulfide	-		3
total	61	61	131

\*: the alloy is partly replaced by PGE sulfide, antimonide, arsenide ()\*: microtextural replacement product of altered Os-Ir-Ru alloy ()\*\*: inclusions in Os-Ir-Ru alloy

dikes found in the serpentinite body, the intrusion of these dikes may have introduced fluids that were rich in S, As, Sb and other highly volatile elements, which may also have led to the formation of postmagmatic laurite, irarsite ( $IrS_2$ ), and an unknown phase whose composition is close to IrSbS (Nakagawa & Ohta 1995).

Although the alloy compositions plot over a wide region of the system Os–Ir–Ru revised by Harris & Cabri (1991), most of them plot along the  $Os_{50}Ir_{50}$ –Ru join (Fig. 5). The regional difference in the mineral assemblage is not reflected in the compositional data



FIG. 4. Photomicrographs of placer PGM. A and B: Optical image of Os-Ir-Ru alloy from Mt. Yubari-dake and Horokanai, respectively, in Hokkaido. Note the hexagonal outline and angular shape. Scale bar, 0.1 mm, reflected light. C and D: Optical and BSE images of Os-Ir-Ru alloy (A) rimmed by an aggregate of irarsite and laurite (IL) from Horokanai, Hokkaido. The area of D is marked in C (white arrowhead). Scale bar; 0.1 mm and 5 µm, respectively. E and F: Optical images of Os-Ir-Ru alloy (A) and laurite from eastern Samar. Note the subrounded shape but still recognizable hexagonal or octahedral outlines of the crystals. Negative hexagonal inclusions in the alloys of E consist of Ir-rich alloy.

for the Os–Ir–Ru alloy. Pt–Fe alloys occur only as inclusions in, or as aggregates with, other PGM phases. Tiny (5–20  $\mu$ m) inclusions of heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>), olivine (Fo<sub>90.5</sub>) and calcic amphibole are occasionally observed in the grains of Os–Ir–Ru alloy, such as in the placer PGM from western Tasmania (Peck *et al.* 1992).

# Eastern Samar

The PGM are composed mainly of a Pt-Fe alloy, but significant amounts of Os-Ir-Ru alloy and sulfides also are present (Table 2). The grains of Os-Ir-Ru alloys and sulfides from Eastern Samar belong to



FIG. 5. Plots on Os-Ir-Ru diagram for the alloy compositions from Hokkaido. The nomenclature (IR: iridium, OS: osmium, RU: ruthenium, RIO: rutheniridosmine) and miscibility gap (shaded) are those of Harris & Cabri (1991).

the smaller size-fraction of the placer materials, and measure up to 1 mm, with the majority being around 0.5 mm in diameter. They exhibit perfectly euhedral to subhedral morphology (Fig. 4E). The grains of Os–Ir–Ru alloy are compositionally homogeneous osmium and iridium, and usually contain less than 10 atomic % of Ru (Fig. 6). Osmium- and iridium-bearing laurite, which also is common, occurs mainly as discrete euhedral grains (Fig. 4F), rarely as minute (<50  $\mu$ m) inclusions within Pt–Fe nuggets (Table 2) and chromite. The bulk of the laurite grains are fairly homogeneous, and contain 19 to 38 wt% of Os, and 3 to 15 wt% of Ir (Fig. 6).

Despite a discrepancy in the size of the grains, the morphology and chemistry of laurite in the placers are similar to those of chromite-hosted laurite in associated ophiolitic bedrock (Franco *et al.* 1993). These grains are thus considered to be magmatic in origin. Some grains exhibit complex microtextures and compositional inhomogeneities, which may be a result of rapid growth in the melt. Mineral inclusions are rather common in laurite, and occur either intermittently or as clusters within a grain. The inclusions are composed mostly of bornite, chalcopyrite and PGE-bearing pentlandite.

#### DISCUSSION

In general, Os, Ir, and Ru (I-PGE) are concentrated in the most refractory cumulates, whereas Rh, Pt, and Pd (P-PGE) behave as incompatible elements and are progressively concentrated in the melt (*e.g.*, Barnes *et al.* 1985, Keays 1995). That is why ophiolites, which are assumed to represent mantle-derived materials, have essentially unfractionated PGE patterns characterized by a relative enrichment of I-PGE and depletion of P-PGE (Barnes *et al.* 1985). Several studies (*e.g.*, Stockman & Hlava 1984, Talkington & Watkinson 1986) have also shown a positive correlation between Cr and I-PGE in ophiolitic chromitites. This is usually manifested by the occurrence of minute inclusions of subhedral to euhedral laurite or Ir-Os-Ru alloy in chromitites. These inclusions are believed to have been



FIG. 6. Plots on Os-Ir-Ru diagram for the alloy composition and laurite from Samar. The nomenclature and miscibility gap (shaded) are those of Harris & Cabri (1991).

trapped as solid crystals during the formation of chromite (Talkington et al. 1984).

The origin of placer PGM, however, remains controversial. Whether the grains are primary magmatic in origin (Cabri *et al.* 1981, Peck *et al.* 1992) or secondary products formed during river transport (Bowles 1986, 1988, Burgath 1988) is still open to argument. But in light of several studies on placer concentrates, many investigators have concurred that Os-Ir-Ru minerals, and especially their alloys, are primary and magmatic in origin (Cabri & Harris 1975, Feather 1976, Bird & Bassett 1980, Hagen *et al.* 1990). Furthermore, osmium isotopic studies on placer Os-Ir-Ru minerals from several localities support this hypothesis (Hattori & Hart 1991, Hattori *et al.* 1992).

As noted above, placer PGM from Hokkaido and Eastern Samar were obtained proximal to the ophiolitic bodies. Their distinct euhedral morphology, such as the prismatic and angular shapes of the Os–Ir–Ru minerals (Fig. 4), suggests little or no effect of abrasion during transport. Clearly, this is indicative of their magmatic origin. The presence of olivine and amphibole inclusions in the minerals also provides evidence for their

magmatic origin. Such magmatic inclusions in placer PGM are known from Western Tasmania (Peck et al. 1992) and Fifield (Slansky et al. 1991), Australia. In the same manner, the spongy textures and inclusions of hydroxides, both suggesting surface environmental products of placer PGM (Cabri et al. 1981, Burgath 1988), are not observed in the Os-Ir-Ru minerals. The alloys and sulfides, particularly in Eastern Samar, show several complex microtextures that can only be related to crystallization at magmatic temperatures (Franco et al. 1993). Therefore, these mineralogical features, coupled with the geological aspects of the two areas. strongly suggest that the Os-Ir-Ru minerals in this study are of magmatic origin. With regards to the preponderance of placer Pt-Fe alloy from Eastern Samar, detailed description of these features and discussion of their genesis will be presented elsewhere.

As mentioned above, two types of regional assemblages of placer PGM from ophiolites are recognized: Os–Ir–Ru alloys without primary laurite (named type H, after Hokkaido), and Os–Ir alloys with associated primary laurite (type S, after Samar). Placer PGM from Burma (Hagen *et al.* 1990) consist mostly of Os–Ir–Ru alloys, which rarely include small grains of laurite. Also, a majority of the PGM from Papua New Guinea consist of Os–Ir–Ru alloys, with minor amounts of small inclusions (Cabri *et al.* 1996) and products of secondary alteration (Harris 1974) of laurite. Laurite-free placer PGM, including Os–Ir–Ru alloys, are recognized in the ophiolite complex of the Aras mountains, Turkey (Cabri *et al.* 1996). These assemblages are rather similar to type-H alloys. In contrast, the osmium and iridium from the Pirogues alluvium, New Caledonia ophiolite complex (Augé & Maurizot 1995), are almost free of Ru. In addition, a large proportion of laurite grains are found associated with chromitite in the area. Thus, this assemblage of PGM corresponds to the type-S alloys.

As mentioned in the introduction, almost all Os-Ir-Ru alloys of placer PGM from southeastern Kalimantan are Ru-poor (Stumpfl & Tarkian 1973, Cabri *et al.* 1996). A number of laurite grains have been detected in chromitite from the Meratus-Bobaris ophiolite, southeastern Kalimantan (Burgath 1988). If the placer concentrate originated from the ophiolite, as Burgath (1988) proposed, this assemblage may also correspond to type S. However, Zientek *et al.* (1992) suggested that those in the southeastern Kalimantan placers were derived from Alaskan-type complexes. Tasmanian placer PGM, including Ru-poor Ir-Os-Ru alloys (Ford 1981) and laurite (Peck & Keays 1990), originated from Alaskan-type intrusions.

These observations, however, are hampered by a lack of data on placer Os-Ir-Ru minerals from other ophiolitic suites. Even the extensive compilation of over one thousand compositions of alloy (Cabri *et al.* 1996) does not include adequate data from other ophiolites, and is not sufficient for a thorough statistical treatment. However, this may well be a start to a new direction of research to enhance our understanding of placer PGM, not only from ophiolites, but also Alaskan-type complexes, and their probable genesis.

The association of an Os-Ir-Ru alloy with laurite within a chromite grain is reported from ophiolites in, for example, Greece (Augé 1985) and New Caledonia (Legendre & Augé 1986). Their microscopic textures suggest epitactic growth of Ru-rich laurite on a euhedral grain of alloy. Thus, crystallization of the alloy must have occurred prior to the formation of laurite. Phase diagrams indicate that melting temperatures of Os-Ir-Ru alloys are between 2443 and 3050°C (Bird & Bassett 1980). Thermodynamic data (Westland 1981) show that laurite is the first PGE sulfide that crystallizes in a cooling magma. On the other hand, Ru-poor alloys that epitacticly grew on euhedral and zoned laurite from ophiolitic chromitites are reported from Quebec (Corrivaux & Laflamme 1990) and Albania (Amossé et al. 1992). The sulfur fugacity,  $f(S_2)$ , in these chromitites is estimated to have been relatively high (between Ru-RuS<sub>2</sub> and Pt-PtS buffers; Amossé et al.

1992). Therefore, it is expected that, under high  $f(S_2)$ , Ru in the magma is consumed during crystallization of laurite, resulting in the formation of a Ru-poor alloy in the later stage, whereas conditions of low  $f(S_2)$  lead to appearance of a Ru-rich alloy in the magma prior to the crystallization of laurite.

Although the original Os–Ir–Ru content of the magma is a principal factor that controls composition of the alloys and laurite, the order of crystallization, as determined by  $f(S_2)$ , may be more important to the Ru content in the alloys. Coexisting alloys and laurite could give information on the  $f(S_2)$  in the magma, but it is very difficult to find a rock-hosted alloy–sulfide pair. Only statistical examination of the paragenetic and compositional data on placer PGM can reveal the regional difference of  $f(S_2)$  in the very early-stage magma responsible for the ophiolite, near its source in the mantle.

### CONCLUSIONS

Two types of assemblage of Os–Ir–Ru minerals of ophiolitic origin are recognized. One type consists of Os–Ir–Ru alloy, which shows a wide range in chemical composition, and is represented by the assemblage in Hokkaido, Japan. Primary laurite is essentially absent in this type of assemblage. The other, Ru-poor Os–Ir– Ru alloy with laurite, is typically observed in Eastern Samar, Philippines. The differences in the assemblages presumably reflect the order of crystallization of the alloy and laurite. As the order largely depends on  $f(S_2)$ in the magma, this difference can be an indicator of  $f(S_2)$  in the ophiolite.

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