

Distribution of platinum-group minerals in ophiolitic chromitites

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This paper reviews the distribution of platinum-group minerals in ophiolitic chromitites. Our data and literature data, obtained by *in-situ* investigation of polished sections and techniques of mechanical separation [hydroseparation (HS), or combining electric pulse disaggregation (EPD) plus HS], are contrasted. Finally, *in-situ* textural data are used as platform criteria to compare the different proposed models that attempt to explain the origin of the platinum-group mineral assemblages found in ophiolitic chromitites.

Keywords: Platinum-group minerals, Ophiolitic chromitites, *In situ* investigation, Mechanical separation

Introduction

Pioneering work from the early 1980's^{19,41,42,64,71,73} showed that ophiolitic chromitites contain significant amounts of platinum-group elements (PGE), though comparatively lower (hundreds of ppb) than chromitites hosted in layered ultramafic–mafic complexes.^{55–57} Platinum-group elements mainly concentrate as specific minerals of these elements known as platinum-group minerals (PGM). The study of PGM assemblages together with the composition of chromite provides us with valuable information regarding the physico-chemical nature of parental melt(s) from which chromitite crystallised.^{2,5,27,29,51,80} A detailed knowledge of these assemblages also provides information regarding the post-magmatic events (e.g. serpentinisation, hydrothermal alteration, metamorphism or weathering) affecting chromitites during, or after, the emplacement of the ophiolitic complexes.^{6,24,30,68,71,74,77}

There now exists an ample body of data on PGM in ophiolitic chromitite. The purpose of this paper is to present the outcome of a statistical study on the distribution of PGM in ophiolitic chromitites taking into account both their abundance and their textural location in chromitite ore bodies. Based on our own research and information from the literature, we contrast data obtained by *in-situ* examination of polished sections and by techniques of mechanical separation [hydroseparation (HS), or combining electric pulse disaggregation (EPD) plus HS]. For this statistical

study, we used data from 23 localities hosted in ophiolitic complexes ranging in age from Proterozoic to Cenozoic. In order to provide an up-to-date picture of the origin of the different PGM assemblages in ophiolitic chromitites, we also contrast different proposed models in the literature, on the basis of their textural location of PGM in the chromitite.

Data selection and methods

We compiled a list of PGM in ophiolitic chromitite worldwide in which the absolute number of grains in the chromitite is reported. For this we took into consideration grains obtained both by *in situ* investigation on polished sections (in which the textural location of PGM is clearly known) and grains obtained by techniques of mechanical separation [hydroseparation (HS), or electric pulse disaggregation (EPD) plus hydroseparation (HS)]. The data base from which we worked included 4678 PGM grains in chromitites from 23 localities belonging to ophiolitic complexes of different age and post-magmatic evolution (Table 1). From a morphological point of view,^{8,28,47,48,59} both podiform and banded chromitites are included. Whereas podiform chromitites occur in mantle tectonites or in the Moho Transition Zone (MTZ), banded chromitites are restricted to the upper levels of the ophiolitic sequence (MTZ and/or mafic–ultramafic crustal cumulates) (Table 1).

Chromitites from which accurate quantitative data of the distribution of PGM are available (Table 1) are hosted in Precambrian ophiolitic complexes (Al'Ays, Saudi Arabia; Pampean Ranges, Argentina; and Bou Azzer, Morocco), in Palaeozoic ophiolitic complexes (chromitites from Shetland Islands, Scotland; Kraubath and Hochgrössen, Austria; Great Serpentine Belt, Australia; Thetford Mines, Canada; Tehuizingo, Mexico; Ray-Iz, Rusia; and Dobromirski, Bulgaria), Mesozoic ophiolitic complexes (chromitites from Troodos, Cyprus; Ohtrys, Vourinos and Pindos, Greece; Omán, Sultanate of Oman; Mugla, Turkey, Moa-Baracoa, Mayari and Sagua de Tánamo, Cuba;

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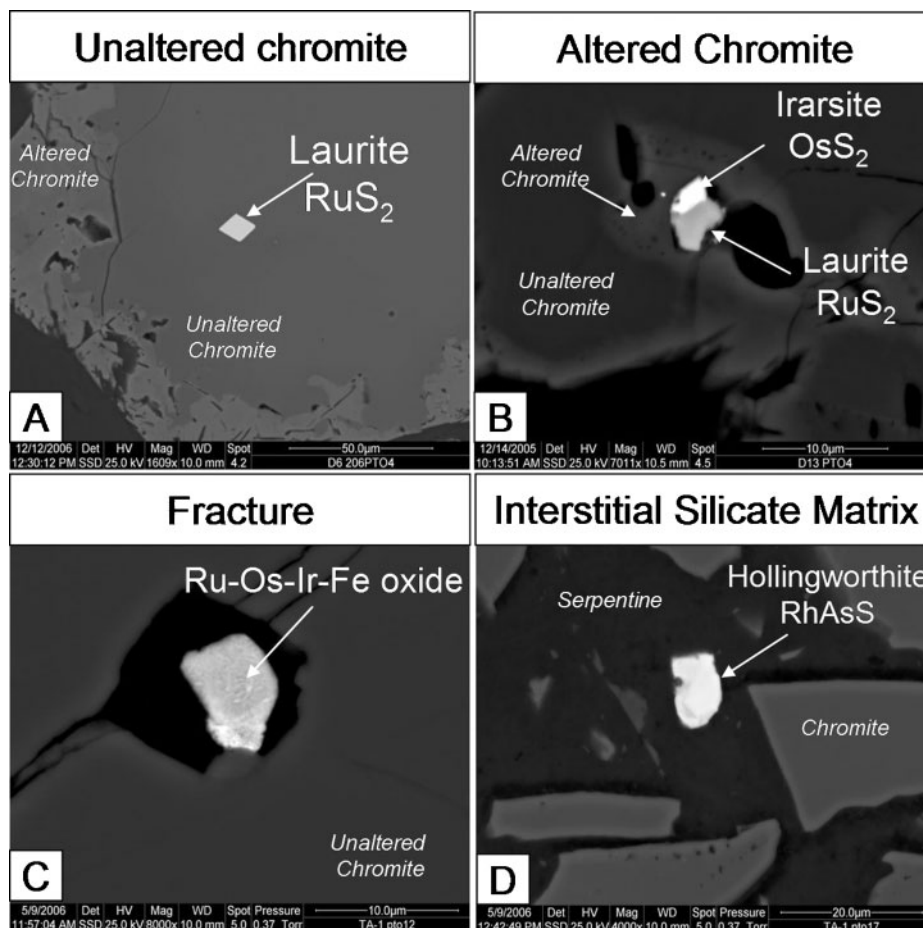
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Table 1 Characteristics of the studied ophiolite complexes. Keynotes: (*) *In situ*, (**) *in situ* plus EPD-HS, Prot: Proterozoic, Pa: Palaeozoic, M: Mesozoic, C: Cenozoic. Hz: Harzburgite, D: Dunitite, Px: Pyroxenite, W: Wehrlites, G: Gabbro, Srp: Serpentinite, MTZ (Moho Transition Zone)

Locality	Country	Age	Host Rock	Type	Alteration	References
Al'Ays(*)	Saudi Arabia	Pro	Mantle tectonites (Hz-D)	Pod	Serpentinisation	66
Pampean ranges(*)	Argentina	Prot	Mantle tectonites (Hz-D-Px)	Pod	Hydrothermal alteration/serpentinisation	67
Bou Azzer(*)	Morocco	Prot	Mantle tectonites (Hz-D)	Pod	Serpentinisation/greenschists	30
Shetland(*)	Scotland	Prot/ Pa	Mantle tectonites (Hz-D)	Pod	Hydrothermal alteration/serpentinisation (?)	61–65, 74
Kraubath(**)	Austria	Prot/ Pa	Cumulates (D-W)	Pod	Amphibolite/greenschist	46–48, 77
			Mantle tectonites (Hz-D-Px)	Pod		
Hochgrosen(**)	Austria	Prot/ Pa	MTZ (Hz-D-Px)	Band		
Ray-Iz(*)	Russia	Pa	Mantle tectonites (Hz-D-Px)	Pod	Serpentinisation/eclogite/amphibolite/greenschist (?)	46, 77
Tehuizingo(*)	Russia	Pa	Mantle tectonites (Hz-D)	Pod		27
Great Serpentinite Belt(*)	Australia	Pa	Mantle tectonites (Srp)	Pod	Eclogite/amphibolite/greenschist	84
			Mantle tectonites (Hz-D)	Pod	Greenschists/serpentinisation	83
Thetford Mines(*)	Canada	Pa	Cumulates (D)	Band		
			Mantle tectonites (Hz-D)	Pod	Serpentinisation	29, 20
Dobromiritsi(*)	Bulgaria	Pa	Cumulates (D)	Band		
Troodos(*)	Cyprus	M	Mantle tectonites (Hz-D-Px)	Pod	Serpentinisation/greenschists/amphibolite	32, 76, this study
Othrys(*)	Greece	M	Mantle tectonites (Hz-D)	Pod	Serpentinisation	50
Vourinos(**)	Greece	M	Mantle tectonites (Hz-Lz-D)	Pod	Serpentinisation	26
Pindos(**)	Greece	M	Mantle tectonites (Hz-D)	Pod	Serpentinisation	4, 5, 24, 38
Oman(*)	Oman	M	Mantle tectonites (Hz-D)	Pod	Serpentinisation	36, 75
			Mantle tectonites (Hz-Py)	Pod	Serpentinisation (?)	2, 5
			MTZ (Hz-D)	Pod		
Mugla(**)	Turkey	M	Cumulates	Band		
Moa-Baracoa(*)	Cuba	M	Mantle tectonites (Hz-D)	Pod	Serpentinisation	80
Mayar(*)	Cuba	M	MTZ (Hz-D)	Pod	Serpentinisation	29
Sagua de Tánamo(*)	Cuba	M	Mantle tectonites (Hz-D)	Pod	Serpentinisation	29
Loma Peguera(**)	Dominican Republic	M	Mantle tectonites (Hz-D)	Pod	Serpentinisation	32, this study
Triébaghi(*)	New Caledonia	C	Mantle tectonites (Hz-Lz-D)	Pod	Serpentinisation	68, 85
Ouen Island(*)	New Caledonia	C	MTZ (D-W-G)	Band	(?)	5, 9
					Hydrothermal alteration/serpentinisation	32, this study



1 Back-scattered electron image of PGM occurring in the different textural positions in ophiolitic chromitites. A and B from chromitites of the Dobromirski Ultramafic Massif (southeastern Bulgaria). C and D from chromitites of the Sagua de Tánamo (eastern Cuba)

and Loma Peguera; Dominican Republic), and Cenozoic ophiolitic complexes (chromitites from Tiébaghi and Ouen Island, New Caledonia).

As shown in Table 1, most podiform chromitites occur in dunite hosted in mantle harzburgite. Likewise, there are podiform chromitites in mantle sequences that consist mainly of harzburgites and lherzolites (Othrys and Tiébaghi). In contrast, banded chromitites frequently occur in crustal dunites (Great Serpentine Belt and Thetford Mines), or are hosted by units of harzburgite, dunite-wehrlite or wehrlite-gabbro of the mantle-crust transition zones as in the Kraubath Massif and in the Ouen Island (Table 1).

Frequency distribution of platinum-group minerals

Platinum-group minerals occur in ophiolitic chromitite as minute solid inclusions (usually less than 30 μm in diameter) with morphologies varying from euhedral to subhedral and anhedral shapes. They may form single or composite (biphase or polyphase) grains made up of PGM solely, or PGM combined with base-metal minerals (e.g. sulphides, arsenides and alloys) or silicates. Platinum-group minerals can be found in four principal textural positions in the chromitites:

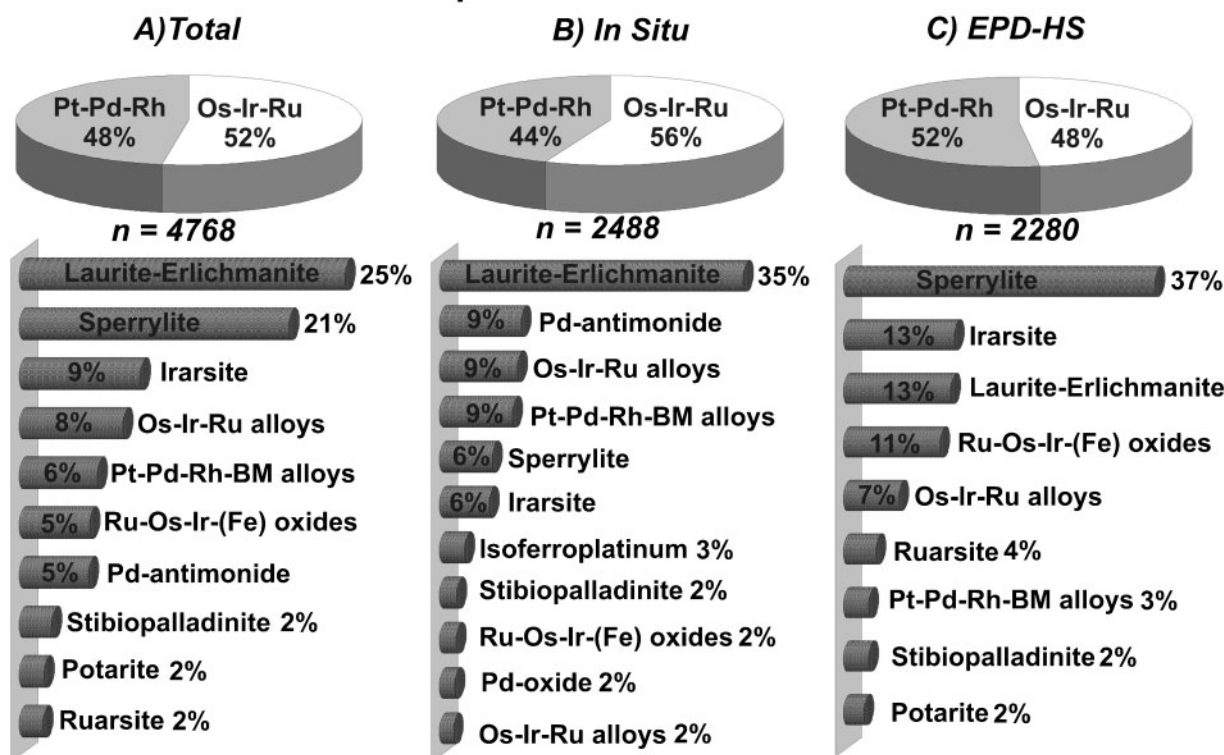
- (i) within unaltered zones of chromite crystals (usually cores)

- (ii) in altered inner zones or edges of chromite crystals
- (iii) in fractures of chromite grains
- (iv) in the interstitial silicate matrix (unaltered or altered) between chromite grains (Fig. 1).

Os-, Ir-, and Ru-rich PGM are relatively more abundant (up to 52%) in ophiolitic chromitites than Pt-, Pd-, and Rh-rich PGM (48%). This includes both podiform and banded (Fig. 2A) types. Based on a number of grains obtained by *in-situ* investigation, Os-, Ir-, and Ru-rich PGM are predominant (56%) (Fig. 2B). In contrast, based on the number of grains recovered by techniques of mechanical separation, ophiolitic chromitites are dominated by Pt-, Pd-, and Rh-rich PGM (52%) (Fig. 2C). However, the latter distribution must be taken with care due to the strong influence of PGM population recovery in Kraubath, where Malitch *et al.*^{46–48} described several grains of Pt-, Pd- and Rh-rich PGM (for example, sperrylite represented close to 37% of all PGM grains). If data from Kraubath are ruled out, it becomes clear that on the whole, PGM mineralogy in ophiolitic chromitites consists mainly of disulphides of laurite (RuS_2)-erlichmanite (OsS_2) solid solution series, Os–Ir–Ru alloys and irarsite (IrAsS), and to a lesser extent, sperrylite (PtAs_2), and Pt–Pd–Rh \pm (base-metals) alloys (Fig. 2A).

In podiform chromitites the distribution of PGM, based solely on the number of grains obtained by *in-situ*

Ophiolite Chromitites



(A) percentage of total grains; (B) percentage of PGM grains recognised *in situ* on polished thin sections; (C) percentage of PGM grain recovery using mechanical separation techniques. EPD: electric pulse disaggregation, HD: hydroseparation

2 Distribution (>2% on the total) of the PGM species in ophiolitic chromitites. PGM-bearing chromitites included in this study are listed in Table 1. (n=number of grains)

investigation on polished sections is dominated by Os-, Ir- and Ru-rich minerals (72%) (Fig. 3A). This further enrichment in Os-, Ir- and Ru-rich PGM is clearly observed in unaltered chromite (up to 93% of Os-, Ir- and Ru-rich PGM). On the contrary, the population of grains found in altered zones (altered chromite, fractures and in the interstitial silicate matrix) is characterised by equal proportions of Os-, Ir- and Ru-rich PGM, and Pt-, Pd- and Rh-rich PGM (50% of each mineral set) (Fig. 3C). The PGM in unaltered chromite mainly consists of the laurite (RuS_2)-erlichmanite (OsS_2) solid solution series (78%), followed by Os-Ir-Ru \pm base-metal alloys (13%) and irarsite (4%). The similarity between the two mineral sets in altered zones is mainly a consequence of the greater abundance of Pt-Pd-Rh \pm base-metal alloys (26%), Os-Ir-Ru \pm base-metal alloys (17%), irarsite (14%), sperrylite (12%) and Ru-Os-Ir-(Fe) oxides (Fig. 3C). The low percentage of minerals of the laurite-erlichmanite solid solution series in the altered zones of the chromitites (7%), relative to their proportion in unaltered chromite (78%), (Fig. 3B and C) is noteworthy.

In banded chromitites, the population of PGM grains recognised *in-situ* is dominated by Pt-, Pd- and Rh-rich PGM (80%) (Fig. 4A). In this case, there are not significant differences between PGM located in altered and unaltered zones of the chromitite (Fig. 4B and C). Platinum-group minerals in unaltered chromite includes sperrylite (31%), isoferroplatinum (Pt_3Fe) (18%), and stibiopalladinite (Pd_5Sb_2) (11%) (very abundant at Kraubath Massif).⁴⁶⁻⁴⁸ The most abundant Os-, Ir- and Ru-rich PGM are also members of the

laurite-erlichmanite solid solution series, irarsite and Os-Ir-Ru alloys (Fig. 4B). On the other hand, the PGM in altered zones of the chromitite are mainly dominated by Pt-Pd-Rh \pm base metals (13%), followed by Pd-oxides (13%), isoferroplatinum (11%), and malanite (CuPt_2S_4) (9%) (the latter, partly desulphurised, specially abundant in the interstitial silicate matrix of chromitites from Ouen Island).³²

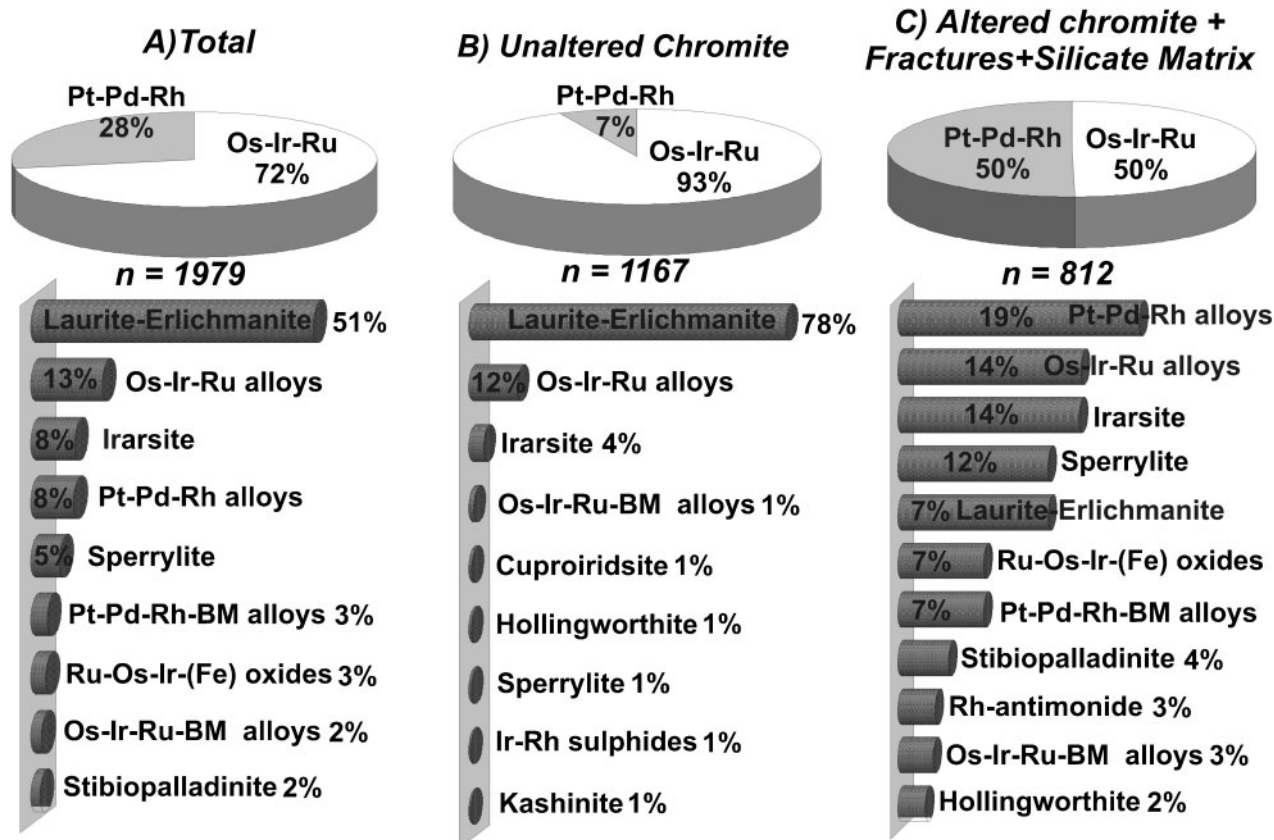
Although here we describe PGM as stoichiometric species, it is worth noting that most of the S-bearing PGM (e.g. sulphides or sulpharsenides) located in altered zones show evidence of alteration (e.g. desulphurisation and/or oxidation).

Discussion

In-situ study of platinum-group minerals on polished sections versus mechanical separation

A comparison of the two techniques of investigation, *in-situ* and mechanical separation, (Fig. 2B and C) reveals a sharp difference between proportions and an unexpected abundance of Pt-, Pd- and Rh-rich PGM. This contrast, that is a consequence of how the data are collected, was first reported in chromitites from the layered complex of Niquelandia by Rudashevsky *et al.*⁷⁰ and, later, in ophiolitic chromitites from Mugla and Loma Peguera by Uysal *et al.*⁸¹ and Zaccarini *et al.*⁸⁵ respectively. This difference can also be observed if we compare the results obtained by different authors reporting findings in Vourinos,^{4,5,24,38} Pindos,^{36,66,75} and Kraubath and Hochgrössen.^{46-48,77} This difference in PGM proportions can be traced to a lower

Podiform Ophiolite Chromitites



(A) percentage of total grains; (B) percentage of PGM included in unaltered chromite; (C) percentage of PGM located in altered chromite, fractures and in the interstitial silicate matrix

3 Distribution (>2% on the total) of the PGM species recognised *in situ* on polished thin sections from podiform ophiolitic chromitites. PGM-bearing chromitites included in this study are listed in Table 1. (n=number of grains)

representativity of results from *in-situ* examination of polished sections than results obtained by techniques of mechanical separation.

The study of concentrates of PGM provides a more complete overall picture of PGM mineralogy in chromite. Likewise, both the number and size rank of the PGM grains are higher.^{36,38,46–48,81,85} However, *in-situ* investigation of polished sections provides more adequate information on the primary or secondary origin of PGM, based on their textural location in the chromite. Moreover, as González-Jiménez³² has recently shown, *in-situ* investigations on polished sections under a field emission scanning microscope (FESEM) allows for the identification of PGM grains with sizes even smaller than 1 µm. However, as has been suggested by other researchers,³⁶ the two methodologies, *in-situ* and concentrate, are complementary and must be used together in order to have an accurate picture of the distribution of PGM in chromitites.

Origin of platinum-group mineral in ophiolitic chromitites

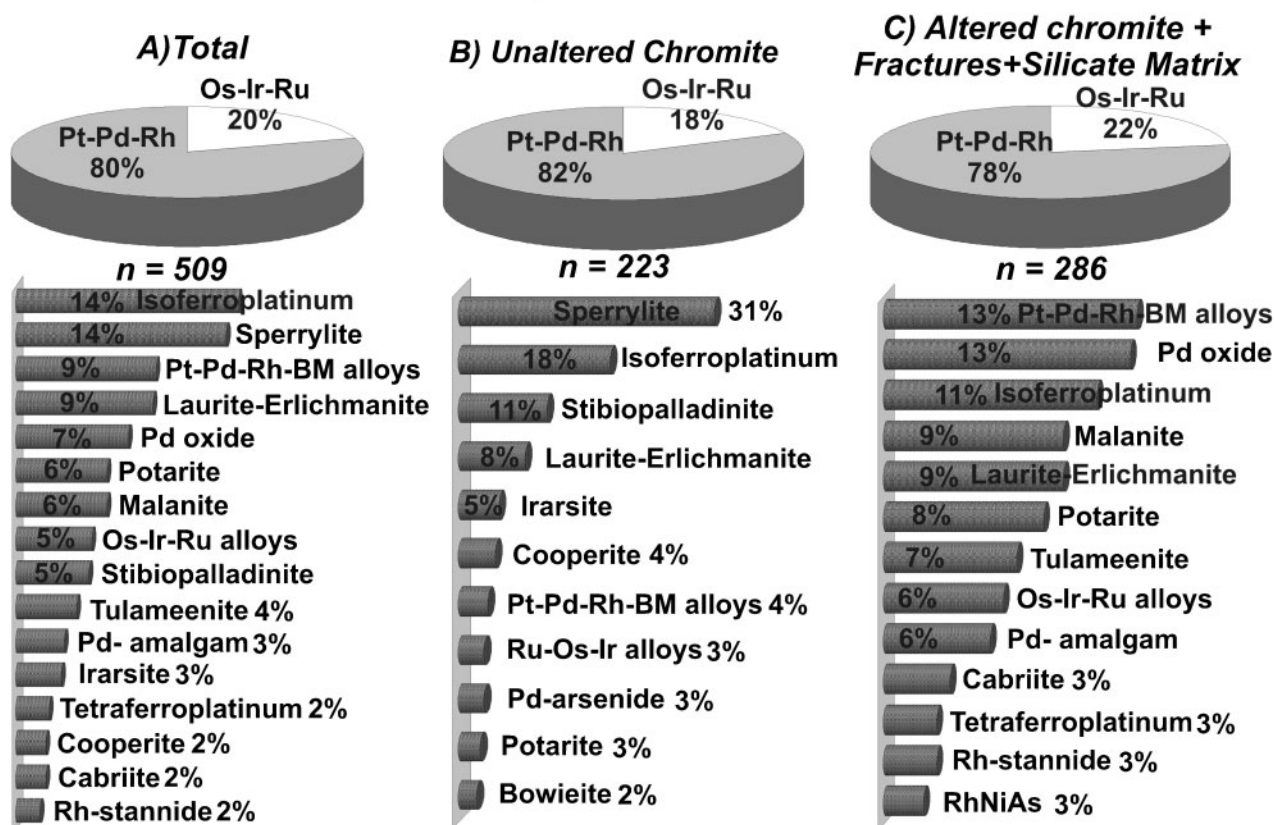
Magmatic origin of platinum-group minerals included in unaltered chromite

Platinum-group minerals mineralogy in unaltered chromite of podiform chromite is clearly dominated (93%) by Os-, Ir- and Ru-rich minerals (mainly laurite-erlichmanite, Os-Ir-Ru alloys and irarsite; Fig. 3B). This suggests that Os, Ir and Ru were fractionated at

earlier magmatic stages, when the chromite crystallised. Gijbels *et al.*³¹ and Naldrett and Cabri⁵⁴ suggested that PGE could fractionate into chromite at high temperatures and on cooling be exsolved from the oxide as discrete PGM grains. This incorporation of Os, Ir and Ru in the chromite lattice has been experimentally tested by Capobianco and co-workers,^{17,18} and Righter *et al.*⁶⁹ and more recently by Locmelis *et al.*⁴⁴ using *in-situ* laser ablation-inductively coupled plasma-mass spectrometry. However, predominant euhedral morphology and heterogeneous distribution of PGM in chromite have led to some investigators^{3,64,71,73} to believe that PGM had to be directly crystallised from melts/fluids before or concurrently with chromite. Empirical observations by Tredoux *et al.*⁷⁸ support the latter interpretation, pointing out that physical trapping of PGM would happen when nano-size metal clusters of PGE (kept in suspension in the melt) were stabilised by the adherence of chalcogenide ligands such as S, As, Sb or Te. According to these authors, if the activity state of chalcogenides is low, the PGE clusters will remain suspended in the silicate melt until they can coalesce to form alloys.

Recent studies by Mungall^{52,53} indicate that the fractionation of PGE was enhanced by small changes in the redox state of the parental melt. Local reduction of the melt could have been created in the boundary layer formed around the crystallising chromite as a consequence of preferential partitioning of Fe³⁺ and

Banded Ophiolite Chromitites



(A) percentage of total grains; (B) percentage of PGM included in unaltered chromite; (C) percentage of PGM located in altered chromite, fractures and in the interstitial silicate matrix

4 Distribution (>2% on the total) of the PGM species recognised *in situ* on polished thin sections from banded ophiolitic chromitites. PGM-bearing chromitites included in this study are listed in Table 1. (n=number of grains)

Cr³⁺ into the oxide, thus causing a saturation of the majority of the PGE oxidised species (Os, Ru and Ir).^{13–15} The insolubilities of Os, Ru and Ir would have taken place in the form of micro-nuggets of alloys of these elements⁵³ which would have remained attached to the chromite edges in equilibrium with the closest melt.^{10,22} Under the appropriate conditions of sulphur fugacity (fS_2), PGE alloys might have reacted with the melt to form sulphides.^{12,39} Thus, as Augé and Johan⁵ and Garuti *et al.*²⁷ suggest, it would be expected that Os, Ir and Ru metallic clusters and alloys formed first, under high temperature and low fS_2 , followed by sulphides of the laurite-erlichmanite solid-solution series upon cooling and increasing fS_2 . However, both experimental-thermodynamic data^{11,12,16,71,82} and empirical observations, such as zoned laurite-erlichmanite coexisting with Os-Ir alloys,^{29,34} suggest that primary PGM could not have formed by fractional crystallisation mechanisms alone but also under variable fS_2 and temperature.

González-Jiménez *et al.*³⁴ suggested that a possible case of heterogeneous physicochemical environment, in which changes of temperature and fS_2 can take place, is when chromite forms during magma mingling of silicate melts in the upper mantle. The turbulent dynamic regiment generated by the mixing of different involved melts within open conduits favour gradients of fS_2 and temperature which can easily explain the common coexistence of sulphides (e.g. laurite-erlichmanite) and alloys (Os-Ir-Ru alloys) apparently in disequilibrium as part of the primary PGM assemblage in many ophiolitic

chromitites. Furthermore, the relative abundance of laurite-erlichmanite suggests that although parental melts of ophiolitic chromitites are S-undersaturated,³⁷ the fS_2 was over the stability limit where only alloys crystallise.² According to the proposed model by González-Jiménez *et al.*³⁴ changes in the chemistry of the parental melt might even allow generation of gradients in As activity. Thus, further increases in As activity rise the formation of the common primary large grains of sulpharsenides as irarsite recognised in many ophiolitic chromitites (Fig. 3B).

On the other hand, data from experiments and natural samples^{10,22,52,53,66} suggest that Pt and Pd would remain in the melt during the crystallisation of chromite and would concentrate later, when temperatures decreased, by PGM crystallising at the borders of chromite and/or the interstitial silicate matrix. In contrast, as a consequence of its intermediate behaviour between Os-Ir-Ru and Pt-Pd,¹⁰ Rh would concentrate by both minerals within the chromite (as evidenced by the abundance of primary hollingworthite) (Fig. 3B) as well as those along the edges of chromite and in the interstitial silicate matrix.

In a recent paper, Prichard *et al.*⁶⁶ pointed out the role of sulphur fugacity as one of the main factors for the concentration of PGE in ophiolitic chromitites. These authors suggested that if a melt is close to sulphur saturation, crystallisation of chromite will increase the potential for sulphur saturation and base metal sulphides and their associated PGE will tend to concentrate

with the chromitite. Practically all the six PGE show the same partition coefficients sulphide melt/silicate melt,^{23,58} hence it would be expected that if sulphur saturation was achieved during early crystallisation of chromite, the chromitite would tend to be enriched in both Os–Ir–Ru- and Pt–Pd–Rh-rich PGM. Sulphur saturation is generally considered rare during the formation of ophiolitic chromitites,⁸ however, González-Jiménez *et al.*³⁴ have recently provided evidence for sulphur saturation. They have found drop-like inclusions of Ni–Cu–Fe sulphides in primary unzoned and zoned laurite-erlichmanite grains associated with grains of a PGE-rich monosulphide solid solution in chromitites from Caridad Mine, Sagua de Tánamo District, eastern Cuba. If the sulphur content in the melt remains below the saturation level (general case), an extensive fractionation between Os–Ir–Ru and Pt–Pd occurs. As a result, Pt and Pd will concentrate in the fractionated melts.^{10,65,66} The fractionated melts may migrate upward giving rise to the Pt- and Pd-rich chromitites occurring in the upper levels of the mantle sequence or basal crustal cumulates.^{4,56,66} Examples of this type of Pt- and Pd-rich ophiolitic chromitites are to be found in Al'Ays,⁶⁶ Shetland Islands,⁶¹ Leka,⁵⁹ Thetford Mines,²⁰ Pindos,^{3,21,75} Kraubath,^{46–48,77} Masif du Sud⁹ and in the Ouen Island, New Caledonia (Table 1).³²

It is well known that As plays a similar role to sulphur as a collector for PGE. The abundance of As-rich PGM (e.g. sperrylite and Pd-arsenide), as part of the primary PGM assemblage in banded chromitites (particularly in Kraubath) (Fig. 4B), indicate that evolved parental melts of Pt- and Pd-rich chromitites, can become enriched in incompatible elements such as As. This conclusion can also be assumed in order to explain the relative abundance of primary Sb- and Hg-rich PGM like stibiopalladinite and potarite (Fig. 4B).

Origin of platinum-group minerals located in the altered zones of chromitites

An in-depth study of the distribution of PGM reveals that some of the most abundant minerals encased in unaltered chromite and interpreted as primary magmatic (laurite-erlichmanite, Os–Ir–Ru ± base-metal alloys, irarsite-hollingworthite, sperrylite, isoferroplatinum and Pt–Pd–Rh ± base metal alloys), also occur in altered zones (Figs. 3B, 3C, 4B and 4C). In contrast, other much less abundant PGM such as Ru–Os–Ir–(Fe)- and Pd-oxides, malanite, tulammenite, Rh- and Pd-rich antimonides, stannides, amalgams and arsenides are exclusively associated with alteration zones of the chromitite (Figs. 3B, 3C, 4B and 4C). A first approach led us to believe that the PGM occurring in altered zones were primary and had been released when chromite underwent post-magmatic alteration. Later, these primary PGM would have been exposed to circulating fluids and as a consequence, would have become unstable, beginning their destabilisation with a modification of their composition (as shown by the partial desulphurisation of some S-bearing minerals such as laurite or malanite), and, in an extreme case, would have become new stable secondary PGM.^{24,83} Some evidences from both our data and literature data support the latter conclusions. These evidences can be summarised as follows:

- (i) both Os–Ir–Ru and Pt–Pd–Rh ± base metal alloys increase their proportions in altered zones of podiform- and banded chromitites respectively (Figs. 3B, 3C, 4B and 4C)
- (ii) PGE-oxides are exclusively associated with alteration zones
- (iii) replacive relationships with the primary magmatic and secondary PGM (sometimes original relicts of the precursor PGE sulphide or arsenide remain in the core of pseudomorphs of the secondary PGE alloy or oxide)
- (iv) radial cracks or spongy textures in secondary alloys/oxides are evidence of the loss of components (mainly S and As).

Although the formation of secondary PGM is still under debate, the aforementioned evidences suggest that they mainly formed by *in-situ* destabilisation of pre-existing PGM. The most general case implies the destabilisation of PGE sulphide or sulpharsenide to give way to a secondary PGE alloy or oxide.^{1,6–9,24,50,62,64,71,74,81,83–85} In the natural system, PGE-secondary alloys are stable under reduced conditions, which can be achieved during earlier steps of serpentinisation,⁷¹ metamorphism,^{33,77,84} or alteration by late-magmatic hydrothermal fluids.^{32,63,74} In contrast, PGE-oxides are closely related to oxidising environments, such as laterisation,^{6–8,85} weathering,^{24,40} or advanced serpentinisation.^{24,35,81}

The mechanism of transformation of a PGM precursor to a PGE secondary alloy is now relatively well known, however, the origin of PGE-oxides is still not totally understood. Uysal *et al.*⁸¹ have recently suggested, along the line of previous works,^{21,24,25,79} that Ru–Fe–Os–Ir oxides in the Mugla ophiolite derive from desulphurisation of laurite at low temperature, with substitution of the removed S by Fe and O. However, textural evidence by González-Jiménez *et al.*³⁵ in chromitites from Sagua de Tánamo, eastern Cuba, suggests that oxides could not be the result of the direct substitution of S by O but that the formation of a precursor secondary alloy is needed. These authors suggest that the oxygen content detected in several grains regarded as PGE-oxides (?) could have been provided by excitation of Fe-oxides (e.g. goethite or hematites) micro-intergrown with PGE (in the metallic state).⁷² These kinds of intergrowths are quite similar to the mustard gold reported in some Au deposits worldwide^{43,45,60} which is made up of an edge of porous native gold in which cavities are occupied by small crystallites of Fe-oxides. This idea is also supported by unpublished data by Hatori *et al.* which demonstrated by means of extended X-ray absorption fine structure technique that in some Pt-oxides from New Caledonia (Pirogues mineralisation),⁶ the oxygen is not combined with PGE but with base-metals (mainly Fe in the form of oxides). These conclusions led us to consider a similar genesis for the PGM oxides as 'mustard gold'. This is also in agreement with microscopic observations by McDonald *et al.*⁴⁹ which describe micro-polycrystalline aggregates made up of the new mineral garutiite (Ni,Fe,Ir), awaruite (Ni₃Fe) and hematites in chromitites from Loma Peguera, Dominican Republic. Furthermore, sub-microscopic particles of chlorite and serpentine have been reported in some of the Ru–Fe–Os–Ir-oxides from the Mugla ophiolite, Turkey.⁸¹ This hypothesis could explain the formation of PGE-oxides

in ophiolitic chromitites (e.g. New Caledonia), in which primary assemblages are dominated by PGE alloys.^{6–9}

As pointed out above, the desulphurisation-oxidation process of pre-existing PGM not only implies loss of anions (e.g. S or As) but also a certain re-mobilisation of PGE.^{24,35,50,68,71,74,81,84} The circulating solutions are able to re-mobilise and transport PGE from pre-existing PGM and to re-precipitate them as new stable phases. The fixing of PGE takes place when such fluids incorporate anions (e.g. As, Sb, Te, Sn, Hg) into the system.³³ This mechanism of neo-formation of secondary PGM has been applied in order to explain the abundant PGE-rich antimonides, stannides, amalgams and arsenides found in altered zones (Fig. 3C and 4C) of some highly altered ophiolitic chromitites (e.g. Shetland Islands,^{61,63,74} Kraubath,^{46–48,77} Pampean Ranges⁶⁷ and Dobromirski³³, see Table 1).

Summary and conclusions

1. This review shows how the PGE mineralogy obtained by *in-situ* investigation on polished sections differs from that obtained by mechanical separation. Although mechanical separation provides a more representative assessment of the PGE mineralogy, textural information is lost. This conclusion led us to suggest, in line with previous investigators, that a combined study of *in-situ* and in concentrate must be used in order to have a detailed knowledge of the distribution of PGM in chromitites.

2. The location of PGM in different textural positions in chromitite is a result of the intervention of both magmatic and post-magmatic events. Whereas PGM encased in unaltered chromite are considered primary, those located in altered zones of the chromitite (altered edges of chromite, fractures and interstitial silicate matrix) are primary equilibrated with circulating-derived fluids, or secondary formed during post-magmatic processes.

3. The origin of primary PGM associated with chromitite is mainly controlled by crystallisation of chromite, sulphur fugacity and temperature in the melt. Early crystallisation of chromite extracts Os, Ir and Ru producing Pt- and Pd-enriched residual melts. Most Os-, Ir- and Ru-rich PGM tend to be concentrated inside chromite crystals having crystallised concurrently with it. In contrast, Pt-, Pd- and Rh-rich PGM tend to predominate on chromite rims and the interstitial silicate matrix suggesting their crystallisation after chromite and at lower temperatures. The separation of the two subgroups of PGE can be disturbed if sulphur saturation is achieved in the melt, in which case chromitites will have practically the same proportions of Os–Ir–Ru- and Pt–Pd–Rh-rich PGM.

4. Secondary PGM in ophiolitic chromitites form by two main mechanisms: *in-situ* alteration of pre-existing PGM and secondary neo-formation during post-magmatic stages. *In-situ* alteration implies destabilisation of S-bearing PGM to form alloys and oxides. In contrast, secondary neo-formed PGM are generated when anions (mainly As, Sb, Te, Sn, Hg) incorporate into the system by circulating solutions, which stabilise the PGE re-mobilised during the replacement reactions.

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