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Invited review article

## Chromitites in ophiolites: How, where, when, why? Part I. A review and new ideas on the origin and significance of platinum-group minerals

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### ABSTRACT

Platinum-group minerals are the dominant control on the budget of platinum-group elements in ophiolitic chromitites. They vary widely in distribution, morphology, chemistry and Os-isotope compositions. Their distribution in different types of chromitites, and different microstructural sites within them may reflect the role of chromite as a physical “collector” of the platinum-group elements during crystallisation of both phases from melts. The platinum-group minerals show significant Os-isotope heterogeneity on the scale of single micrometric grains enclosed within individual chromite grains. This micro-scale isotopic heterogeneity, and their random spatial distribution within the chromites, argue strongly against an origin of the platinum-group minerals via exsolution from the chromite lattice during post-magmatic cooling.

A re-interpretation of their microstructures and Os isotopes analysed *in situ* had led us to review the traditional models, and to propose several origins for the platinum-group minerals in chromitites. (1) The suites of platinum-group minerals mainly record crystallisation during mixing of multiple different melts and physical entrapment in chromite. (2) Some platinum-group minerals in chromitites may have been scavenged from wall-rock peridotite during migration of the parental melts of the chromitite. (3) Other platinum-group minerals may have precipitated from metasomatic fluid/melts that infiltrated existing chromitites. The recrystallization of pre-existing platinum-group minerals during polyphase metamorphism or “recycling” of the chromitite into deeper mantle levels can explain the presence of micrometric platinum-group minerals with distinct Os-isotope compositions.

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## 1. Introduction

Ophiolites provide direct samples of the mantle–crust beneath oceanic spreading centres, in either mid-ocean or arc-related settings, and can supply unique information about the formation and destruction of oceanic crust and mantle. The mantle sections and the crust–mantle transition zone of many ophiolites contain *bodies* of (Cr, Al)-rich spinel or chromitites (Ahmed and Arai, 2002; Augé and Johan, 1988; Leblanc, 1995; Leblanc and Nicolas, 1992; Leblanc and Violette, 1983; Graham et al., 1996; Melcher et al., 1997; Pagé and Barnes, 2009; Prichard et al., 2008; Rollinson, 2008; Uysal et al., 2009). These chromitites may contain unusually high concentrations of the Platinum Group Elements (PGE: Os, Ir, Ru, Rh, Pt, Pd) (Ahmed and Arai, 2002; Economou-Eliopoulos, 1993; Gauthier et al., 1990; Gervilla et al., 2005; Ismail et al., 2010; Kocks et al., 2007; Leblanc, 1991; Malitch et al., 2001; Prichard et al., 1986, 2008; Thalhammer et al., 1990). These elements, through their diversity of chemical and mineralogical behaviour, can provide unique insights into the crystallisation processes, while their Re–Os isotopic systematics carry information on the history of their mantle sources (e.g. Malitch et al., 2003; Pearson et al., 2007; Walker et al., 2005).

Ophiolites, chromitites and their PGE and Re–Os isotopes thus can help to understand first-order questions about the evolution and geodynamic processes of the lithosphere and possibly the convecting mantle. This paper presents Part 1 of a review of the origin of chromitites (Part 2 is González-Jiménez et al., *this volume*). This study provides benchmark for the re-evaluation and interpretation of the origin of chromitites and thus contributes to a better understanding of the “Lithosphere and Beyond”.

In ophiolitic chromitites, the platinum-group elements reside mainly in specific minerals known as the platinum-group minerals (PGMs), and are to a lesser extent dissolved in base-metal minerals (including Fe–Ni–Cu sulfides, arsenides) and alloys (Ahmed, 2007; Ahmed and Arai, 2003; Augé, 1985; González-Jiménez et al., 2009a; Gutierrez-Narbona et al., 2003; Legendre, 1982; Malitch et al., 2001, 2003; Melcher et al., 1997; Prichard et al., 1986, 2008; Stockman and Hlava, 1984; Tarkian et al., 1991 and references therein). However, despite a great body of work, the links between the PGMs (and their associated base-metal minerals) and formation of their host chromitites are still unclear and hotly debated, as exemplified by continual profusion of experimental studies (e.g. Ballhaus et al., 2006; Finnigan et al., 2008; Mungall, 2005) and empirical works (e.g. Economou-Eliopoulos et al., 2009; Kapsiotis et al., 2012; Pagé et al., 2012; Rajabzadeh and Moosvinasab, 2012).

The main hypothesis proposed in the early 1970s was that the platinum-group elements “dissolve” in the lattice of chromite at high temperature and are later exsolved during cooling as discrete PGMs (Gijbels et al., 1974; Naldrett and Cabri, 1976). Later in the 1980s, many researchers interpreted the PGMs as having crystallised before or contemporaneously with the chromite and then been incorporated into the chromite as solid inclusions (Augé, 1985; Constantinides et al., 1980; Legendre, 1982; Stockman and Hlava, 1984). This later idea, extensively discussed in the context of microstructural observations has been the most accepted during the last three decades (Ahmed, 2007; Augé et al., 1998; Gervilla et al., 2005; Gutierrez-Narbona et al., 2003; Neziraj, 1992; Prichard et al., 2008; Rajabzadeh and Moosvinasab, 2012; Tarkian et al., 1991; Thalhammer et al., 1990; Torres-Ruiz et al., 1996).

A major breakthrough in our understanding of the relationships between chromitites and their enclosed PGMs has come in the last few years, through the analysis of Os isotopes by laser-ablation ICPMS analysis. This technique allows the high-precision in situ

analysis of the Os-isotope compositions of single tiny PGMs (and larger base-metal sulfides). Now the Os-isotope composition of individual PGMs can be directly related to their microstructural setting, internal structure and bulk composition. This has provided new insights into crystallisation processes, and provided new constraints on genetic models. The observation that the Os-rich PGMs in ophiolitic chromitite might have several distinct origins is relevant to our understanding of the Os isotopic evolution of the Earth, and hence to our current models of mantle evolution.

In this work, we combine recent results obtained in experiments on the crystallisation of PGM with chromite (Andrews and Brennan, 2002; Ballhaus et al., 2006; Bockrath et al., 2004a,b; Brennan and Andrews, 2001; Brennan et al., 2012; Finnigan et al., 2008; Fonseca et al., 2012; Mungall, 2005) with data obtained by the in situ analysis of PGEs in chromite (e.g. Pagé et al., 2012) and Os isotopes in individual PGMs, from own work and the literature (Ahmed et al., 2006; González-Jiménez et al., 2012a,b, 2013; Malitch, 2004; Malitch et al., 2003; Marchesi et al., 2011; Shi et al., 2007), to re-examine the models previously suggested for the origin of the PGMs in ophiolitic chromitites and to propose alternative explanations. We attempt to clarify how the PGMs form and why they are found in the chromitites.

## 2. Petrological features of chromitite-hosted platinum-group minerals

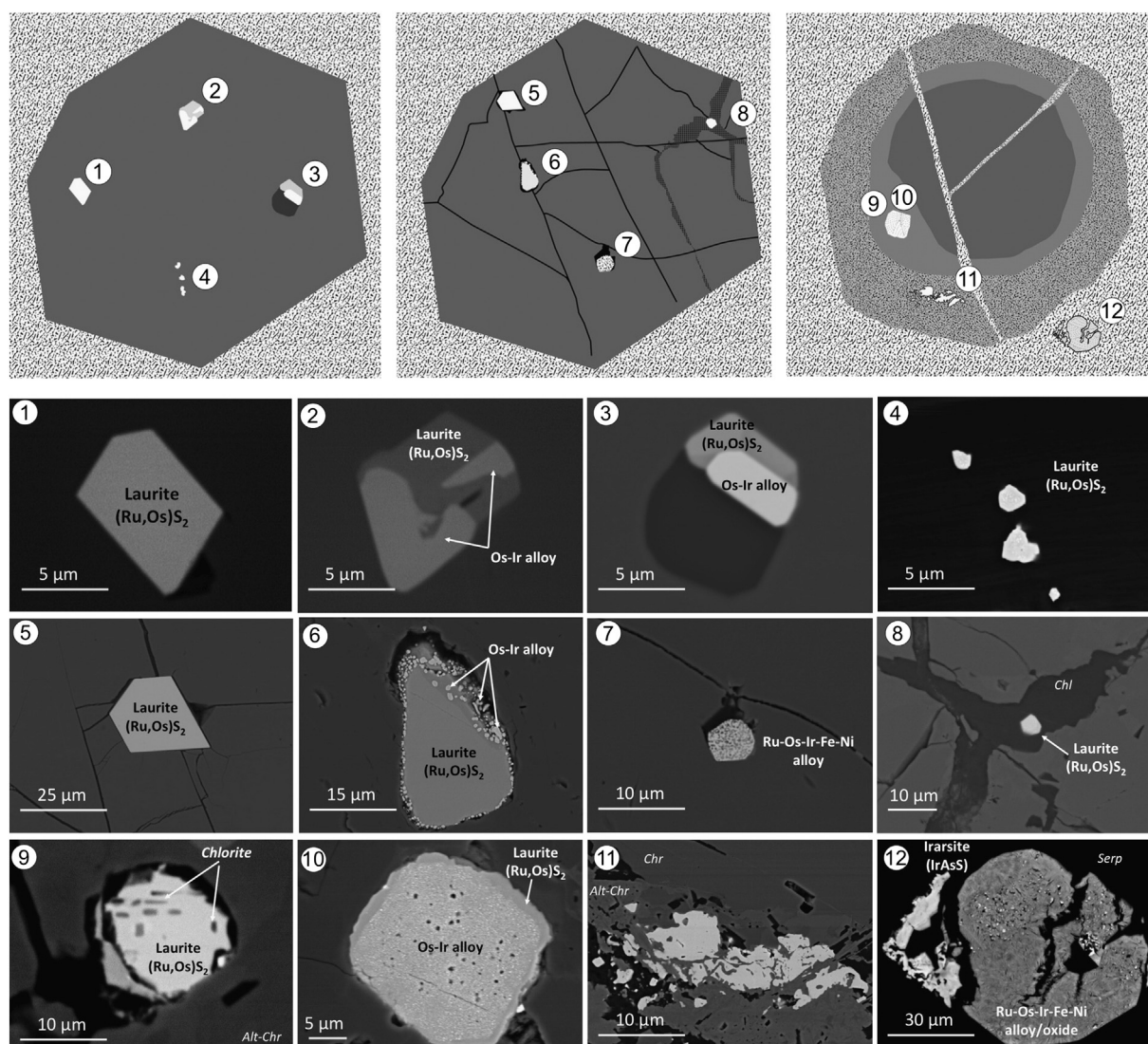
### 2.1. Mode of occurrence and microstructural sites of platinum-group minerals

In a review of platinum-group minerals in ophiolite chromitites, González-Jiménez et al. (2009a), showed that in these types of rocks they are rare minerals, usually less than 30 µm across. They may form single or composite (diphase or polyphase) grains made up solely of PGMs, or PGMs ± base-metal minerals ± silicates, randomly dispersed in larger chromite grains (Fig. 1-1 to -11), or less commonly in the interstitial silicate matrix (unaltered or altered) between the chromite grains (Fig. 1-12). These authors observed that within a single chromite grain, the PGMs can be found in three principal microstructural positions.

- (1) Unaltered zones, mostly in the cores (Fig. 1-1 to -3).
- (2) Open fractures, rarely with irregular outlines and/or alteration rims and/or filled by secondary silicates (Fig. 1-5 to -8).
- (3) Altered inner zones or edges (consisting of ferrous or ferric chromite with either homogenous or porous textures; Fig. 1-9 to -11).

In this study we recognise a fourth microstructural site, inclusion trails. The PGMs may be found in planar arrays (linear trails in section) made up of PGMs ± base-metal minerals ± silicates ± fluid/melt inclusions, which might correspond to former grain boundaries or healed fractures; these inclusion trails can be observed in both unaltered and altered zones within chromite grains (e.g. Fig. 1-4).

Generally, the PGMs that occur within unaltered zones of the chromite are euhedral with polygonal sections (Fig. 1-1 to -3); they rarely are subhedral or anhedral. In contrast, the PGMs associated with open fractures or altered zones of the chromitite may show a wide range of morphologies depending on the degree of mechanical deformation or reaction with secondary fluids (Fig. 1-5 to -12). In the sequence of alteration of a pre-existing PGM, there is an initial partial corrosion along grain boundaries, which may also imply the



**Fig. 1.** Top row – schematic cartoons illustrating microstructural environments in chromite grains (see details in the text). Pictures 1–12 – backscattered electron scanning images of PGM in the indicated microstructural settings. Pictures 1–12 are back-scattered electron scanning images showing morphology, microstructures and mineral assemblages of the platinum-group minerals in chromitites from different ophiolites. 1, 2 and 9 are from chromitites of the Dobromirski Ultramafic Massif, Bulgaria; 3–5 and 8 are from the chromitites from ultramafic complexes of the Vizcaino Peninsula, Baja California Sur (Mexico), 6–7 and 10–11 are platinum-group minerals from chromitites of Loma Baya, Guerrero State (Mexico), 12 are platinum-group minerals from chromitites of the Sagua de Tánamo district, Mayari-Baracoa ophiolite (Cuba).

reaction and release of components and their reprecipitation nearby (e.g. Fig. 1–6). In extreme cases this alteration evolves to inner spongy textures, especially in the case of secondary platinum-group alloys or oxides (e.g. Fig. 1–7 and -12). Grains of PGMs that have recrystallised during post-magmatic alteration may fill pores in porous chromite (Fig. 1–10), commonly coexisting with secondary silicates (e.g. chlorite; Fig. 1–9 and -11). The PGMs occurring in inclusion trails commonly are euhedral but they may also show complex shapes controlled by the cavities they are filling, or by healing of the fractures (Fig. 1–4). Sometimes these grains are altered, with corroded faces or spongy textures due to their reaction with alteration fluids, distinct from those that have precipitated the PGMs.

## 2.2. Frequency distribution of platinum-group minerals

González-Jiménez et al. (2009a) compiled a list of platinum-group minerals in ophiolitic chromitites worldwide in which the absolute number of grains was reported. Unfortunately not many studies published since then include any detailed statistics on the distribution of each PGM species within the different microstructural positions in the

chromitite. Thus, for this work we only report grains identified in situ on polished samples of chromite that allow a clear identification of the microstructural location of the PGM (Supplementary Table 1).

The distribution of platinum-group minerals in chromitites from ophiolites is reported in terms of Type I and Type II chromitites as defined by González-Jiménez et al. (this volume). In this new classification, Type I includes chromitites that, independently of their morphology, host rock and localisation in the ophiolite sequence, show bulk-rock enrichment in Os, Ir and Ru (i.e. IPGE) relative to Rh, Pt, and Pd (i.e. PPGE). Type II includes chromitites that also may show a range of morphologies and are usually localised in the shallower zones of the oceanic lithosphere: their common feature is a significant enrichment in the incompatible PPGEs, and they usually show higher total PGE contents than Type I.

In this work, we have used the definition of ophiolite by Dilek and Furnes (2011), who distinguished six types: Continental margin, Mid-ocean-ridge, Plume, Suprasubduction-zone, Volcanic-arc and Accretionary, which also includes some subtypes. Thus, chromitite-bearing ophiolites that were not considered by González-Jiménez et al. (2009a) are now included in this dataset. Two new localities with chromitites



that are currently being studied by the GEMOC team (Loma Baya and Vizcaino) have been also included in this work. Brief locality descriptions are given in the Supplementary Table 1.

The investigation of platinum-group minerals in situ on polished samples of Type I chromitites shows that these minerals are preferentially located in the *unaltered zones* (cores or inclusion-trails) of larger chromite grains (63%) rather than along their altered edges or open fractures and in the interstitial silicate matrix (hereafter grouped as *altered zones* of the chromitites) (Fig. 2). The Os–Ir–Ru minerals dominate the population: 96% in unaltered chromite and 52% in the altered zones, which is consistent with the enrichment in IPGEs in whole-rock samples of Type I chromitites.

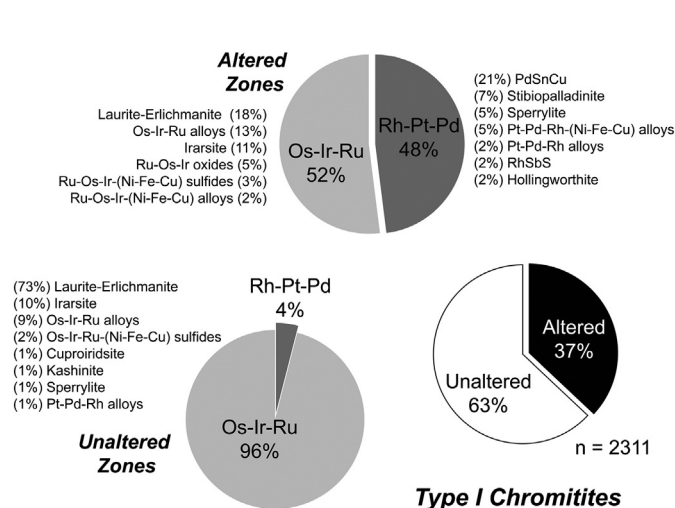
The remarkable enrichment in Os–Ir–Ru minerals in the unaltered zones is mainly due to the presence of abundant disulfides of the laurite (RuS<sub>2</sub>)–erlichmanite (OsS<sub>2</sub>) solid solution series (73%), irarsite (IrAsS) (10%) and Os–Ir–Ru alloys (9%). Most of the remaining Pt-, Pd- and Rh-rich minerals found in these unaltered zones are grains of sperrylite (PtAs<sub>2</sub>) and Pt–Pd–Rh alloys (Fig. 2). Laurite–erlichmanite (18%), Os–Ir–Ru alloys (13%) and irarsite (11%) are also the most abundant Os–Ir–Ru minerals in the altered zones where they are also accompanied by Ru–Os–Ir–(Fe) oxides (5%), which are exclusively found in these microstructural positions (Fig. 2). These oxides often occur as rims around larger grains of laurite–erlichmanite or irarsite, which may also show inner radial cracks or spongy textures and/or S-deficiency. These assemblages and microstructures appear to be produced by the in situ destabilisation of pre-existing Os–Ir–Ru sulfides or sulfarsenides to yield a secondary platinum-group alloy or oxide (Augé and Legendre, 1994; Garuti and Zaccarini, 1997; González-Jiménez et al., 2010, 2011a,b; Proenza et al., 2007; Stockman and Hlava, 1984; Uysal et al., 2009).

This general sequence implies an initial stage in which the platinum-group sulfide or sulfarsenide partially loses S, which may be counterbalanced by the uptake of Fe, Ni or Cu. This is followed, in extreme cases, by complete replacement of the original PGM by a new stable alloy or oxide, depending on the redox conditions. Often these platinum-group alloys are associated with Ni–Fe alloys ± magnetite indicative of very reduced conditions (<–38 log fO<sub>2</sub> at ≤350 °C; Frost, 1985), which can be achieved during the earlier stages of serpentinisation (Garuti and Zaccarini, 1997; González-Jiménez et al., 2011a,b; Stockman and Hlava, 1984), metamorphism (González-Jiménez et al., 2010; Proenza et al., 2008; Thalhammer et al., 1990; Zaccarini et al., 2005) or alteration by late-magmatic hydrothermal fluids (González-Jiménez et al., 2011a; Prichard and Tarkian, 1988; Tarkian and Prichard, 1987). In contrast,

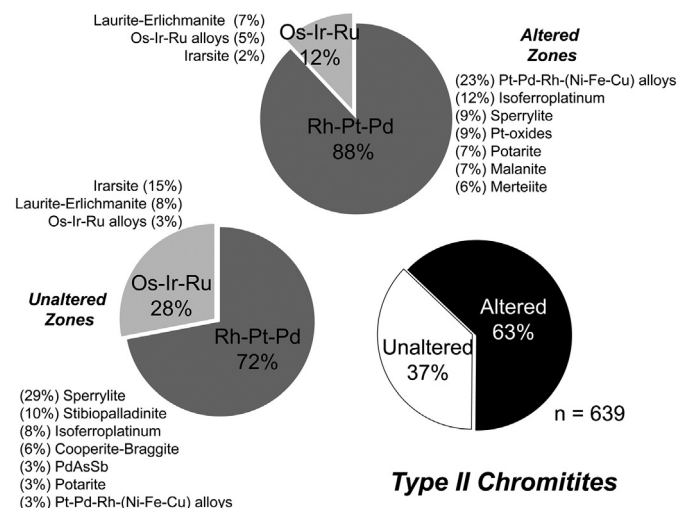
the origin of platinum-group oxides is associated with the circulation of low-temperature oxidising fluids associated with weathering (Augé and Legendre, 1994; Augé and Maurizot, 1995; Augé et al., 1998; Zaccarini et al., 2009) or advanced stages of serpentinisation (González-Jiménez et al., 2011b; Uysal et al., 2009).

The other Pt–Pd–Rh minerals found in the altered zones of the chromitites are stannides, amalgams and arsenides, which are very rare as inclusions in chromite but very abundant in the altered zones of some metamorphosed chromitites, such as the Great Serpentine Belt in Australia (Yang and Secombe, 1993), Kraubath in Austria (Malitch et al., 2001; Thalhammer et al., 1990), the Pampean Ranges in Argentina (Proenza et al., 2008) or Dobromirski in Bulgaria (González-Jiménez et al., 2010). The higher proportion of these platinum-group minerals in the altered zones of those chromitites may reflect the efficiency with which chromite can fractionate the IPGE (producing preferential concentration of PPGE in the interstitial matrix; Ballhaus et al., 2006), from which they are later re-distributed during the invasion of post-magmatic hydrothermal fluids carrying anions (e.g. As, Sb, Te, Sn, Hg) that can fix the PPGE (Ghorfi et al., 2008; González-Jiménez et al., 2010; Thalhammer et al., 1990). The intervention of a secondary fluid also is indicated in many cases by the close association between these platinum-group minerals and the secondary silicates (e.g. chlorite) that fill pores in the altered edges of chromite grains, or occur in open fractures or the interstitial silicate matrix.

The mineralogy Type II chromitites is dominated by Pt–Pd–Rh minerals, which is consistent with their higher contents of those PGEs (Fig. 3). In this type of chromitite, there are more grains of platinum-group minerals in the altered zones (63%) than in the unaltered chromite (37%). Sperrylite (29%), stibiopalladinite (Pd<sub>5</sub>Sb<sub>2</sub>) (10%) and isoferroplatinum (Pt<sub>3</sub>Fe) (8%) and members of the solid solution cooperite (PtS)–braggite (PdS) are the most common minerals in the unaltered zones (Fig. 3); they are particularly abundant in the chromitites of Kraubath (Supplementary Table 1). In contrast, the Pt–Pd–Rh ± base metal alloys (23%), followed by isoferroplatinum (12%), sperrylite (9%) and Pt-oxides, potarite (PdHg) and malanite (CuPt<sub>2</sub>S<sub>4</sub>), are the most abundant platinum-group minerals in the altered zones (Fig. 3). In chromitites like the hydrothermally altered ones of Ouen Island (New Caledonia), grains isoferroplatinum associated with serpentine preserve their perfect magmatic euhedral morphology and compositions, suggesting that they were stable under the highly reducing conditions associated with the formation of serpentine. However, when isoferroplatinum is embedded in a chlorite-rich matrix it shows



**Fig. 2.** Frequency distribution of the platinum-group minerals in Type I chromitites. The dataset of 2311 grains was collated from the chromitites of 30 ophiolite localities (Supplementary Table 1). Note that only platinum-group mineral species with abundances > 2% were listed, except for grains located in unaltered zones.



**Fig. 3.** Frequency distribution of the platinum-group minerals in Type II chromitites. The dataset of 639 grains was collated from the chromitites of 30 ophiolite localities (Supplementary Table 1). Note that only platinum-group mineral species with abundances > 2% were listed except for grains located in unaltered zones.

corroded outlines and is residually enriched in Pd, indicating its destabilisation at higher  $fO_2$ . In contrast, malanite loses S during the formation of serpentine and is oxidised by the fluids that precipitate chlorite (González-Jiménez et al., 2011a). In these two microstructural positions, the remaining Os–Ir–Ru minerals are those that predominate in the Type I chromitites: laurite–erlichmanite, Os–Ir–Ru alloys and irarsite. As observed in Type I chromitites, when these IPGE-rich sulfides are in the altered silicate matrix they commonly show evidence of post-magmatic desulfurisation or oxidation, such as corroded outlines, S-deficiency or rims of platinum-group alloys/oxides.

### 3. Re–Os isotopes of individual grains of platinum-group minerals

The Re–Os isotopic composition of platinum-group minerals in ophiolites was initially examined in detrital grains collected in placers from rivers draining the ultramafic massif of the ophiolites of Kalimantan in Borneo, Hokkaido in Japan and SW California and NW Oregon in the USA (Brandon et al., 2006; Coggon et al., 2011; Hattori and Hart, 1991; Hirata et al., 1998; Meibom and Frei, 2002; Meibom et al., 2002, 2004; Pearson et al., 2007; Walker et al., 1997, 2005) or separated from chromitites (Malitch, 2004; Malitch et al., 2003; Shi et al., 2007; Walker et al., 1996). Platinum-group minerals not liberated from host chromite were analysed for the first time on polished sections by Ahmed et al. (2006) using an ion microprobe, and more recently by the GEMOC team in Australia using laser-ablation multicollector ICPMS (González-Jiménez et al., 2012a,b; Marchesi et al., 2011; this study). We will discuss only the Os isotopic compositions of grains identified from chromitites. These data are compiled in Fig. 4.

Walker et al. (1996) used N-TIMS to analyse a grain of laurite separated from a chromite in the Outokumpu ophiolite, Finland. The grain has sub-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  of  $0.11218 \pm 0.00004$ , corresponding to a  $T_{\text{MA}} \approx T_{\text{RD}}$  model age of 2.23 Ga (Fig. 4) (uncertainties are given at  $2\sigma$ , and 0.1281 is the present-day  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the Enstatite Chondrite Reservoir (ECR); Walker et al., 2002). Most platinum-group minerals from ophiolitic chromitites have very low Re/Os; therefore hereafter we will only report  $T_{\text{RD}}$ .

Malitch et al. (2003) and Malitch (2004) used LA-MC-ICPMS and N-TIMS to measure the Re–Os isotopic composition of individual laurite–erlichmanite ( $\pm$ irarsite  $\pm$ ruarsite) grains liberated from chromitites of the Kraubath (Type I and Type II chromitites) and Hochgrössen (Type I chromitites) massif, Austria. At Kraubath, laurites from Type I chromite (sample K-142) have sub-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.11249 \pm 0.00062$  to  $0.12437 \pm 0.0005$ ;  $n = 16$ ), whereas laurites of Type II chromitites (sample K-134) have supra-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.1308 \pm 0.00011$  to  $0.13212 \pm 0.00065$ ;  $n = 2$ ; Fig. 4).

Laurites of Type I chromitites yield  $T_{\text{RD}}$  from 2.2 to 0.5 Ga (with age peaks at 0.6, 1.1, 1.6 and 2.2 Ga), whereas laurites of Type II yield meaningless future ages ( $-0.39$  to  $-0.58$  Ga). The two grains of laurite analysed from the Type I chromitites from Hochgrössen show  $^{187}\text{Os}/^{188}\text{Os}$  that roughly overlap that of laurites of Type I chromitites from Kraubath,  $0.11940 \pm 0.00059$  and  $0.12392 \pm 0.00164$  (Fig. 4), corresponding to  $T_{\text{RD}}$  of 1.23 and 0.59 Ga respectively.

Shi et al. (2007) carried out in situ Re–Os isotopic analysis on 170 grains of Ru–Os–Ir alloys separated from Type I chromitites of the Luobusa and Dongqiao ophiolites, Tibet. On the basis of their PGE and Os-isotopic compositions they defined two groups of alloys (Fig. 4). Group I ( $n = 145$ ), found in both ultramafic bodies, is characterised by fractionated PGE patterns and homogenous  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.12622 \pm 0.00004$  to  $0.12670 \pm 0.00004$ ) yielding  $T_{\text{RD}}$  between 199 and 268 Ma, with age peaks at 233 Ma in Luobusa and 243 Ma in Dongqiao. They interpreted this group of alloys as early cumulate phases formed during crystallisation of melts. Group II (only in Dongqiao,  $n = 25$ ) has smooth PGE patterns and a much larger range of less radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.12010 \pm 0.00004$  to  $0.12641 \pm 0.00008$ ) yielding  $T_{\text{RD}}$  between 1130 and 240 Ma, with age peaks at  $\sim$ 870, 930, 1089, 1100 and 1130 Ma. They interpreted this group of alloys as formed by the breakdown of residual sulfides during partial melting events in the mantle.

Ahmed et al. (2006) reported significant dispersion of  $^{187}\text{Os}/^{188}\text{Os}$  among grains of laurite within single Type I chromitites in the Proterozoic ophiolites of the Eastern Desert, Egypt and in the Phanerozoic Oman ophiolites (Fig. 4). The sixteen laurites analysed in chromitites from the Eastern Desert have sub-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.1192 \pm 0.0011$  to  $0.1260 \pm 0.0016$ ) but one is supra-chondritic ( $0.1293 \pm 0.0015$ ). Positive  $T_{\text{RD}}$  ranges from 1.3 to 0.3 Ga (Fig. 4). Most analysed platinum-group minerals (36/42) in the Oman chromitites have  $^{187}\text{Os}/^{188}\text{Os}$  higher than the ECR ( $0.1283 \pm 0.0031$  to  $0.1460 \pm 0.0007$ ) and give future model ages. The remaining six grains with sub-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.1208 \pm 0.0011$  to  $0.1280 \pm 0.0004$ ) yield  $T_{\text{RD}}$  ages from 1.03 to 0.01 Ga (Fig. 4). Laurites in chromitites from the MTZ in the Oman ophiolites have a wider range of variation in  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.1280$  to  $0.1460$ ;  $n = 6$ ) than those in chromitites from the deeper in the mantle section. The latter chromitites can be either concordant (i.e. PGE-poor, 0.1390 to 0.1374;  $n = 4$ ) or discordant with their host peridotite (i.e. PGE-rich, 0.1230 to 0.1377).

González-Jiménez et al. (2012a) and Marchesi et al. (2011) analysed a greater variety of PGMs (laurite–erlichmanite, PGE-rich monosulfide solid solution, Ru–Os–Ir–Fe–Ni alloy) and associated base-metal sulfides (millerite, heazlewoodite, pentlandite) in situ on polished thin sections of chromitites from the Mayarí-Baracoa Ophiolite, Cuba (Fig. 4). They showed that on average the PGMs

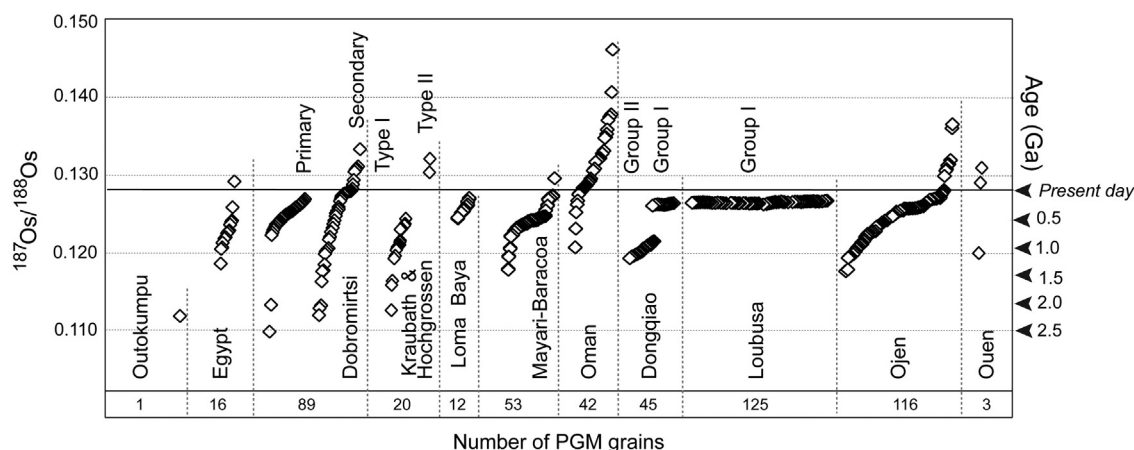


Fig. 4. Os-isotope compositions of platinum-group minerals analysed in situ in chromitites from ophiolite-type ultramafic complexes. Updated after Malitch et al. (2003) and Malitch (2004); the provenance of the data is given in the text.

have slightly more radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.1185 \pm 0.002$  to  $0.1295 \pm 0.0009$ ; average =  $0.1242$ ,  $n = 45$ ) than the associated base-metal sulfides ( $0.1203 \pm 0.0004$  to  $0.1251 \pm 0.0003$ ; average =  $0.1228$ ,  $n = 25$ ), but both have low  $^{187}\text{Re}/^{188}\text{Os}$  (0.08; the present-day value of the chondrite is 0.421; Walker et al., 2002). Most PGMs yield positive  $T_{\text{RD}}$  from 1.4 to 0.10 Ga. González-Jiménez et al. (2012a) reported that in the Caridad chromitite body, where laurite coexists with abundant BMS, the  $T_{\text{RD}}$  of the laurites covers a much wider and younger range of model ages (0.10 to 0.78 Ga; mean =  $0.50 \pm 0.15$  Ga) than those of the base-metal sulfides (0.43 to 1.13 Ga; mean =  $0.78 \pm 0.18$  Ga). Significant variations in  $^{187}\text{Os}/^{188}\text{Os}$  occur among sulfide grains forming parts of single aggregates smaller than 50  $\mu\text{m}$  in diameter, or within a single chemically and isotopically zoned PGM (González-Jiménez et al., 2012a). For example, in the composite grain of Fig. 5a, the PGE-rich Mss has more radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ( $0.1273 \pm 0.0016$ ) than the associated laurite ( $0.1245 \pm 0.0001$ ). Similarly, in the large grain of laurite in Fig. 5b the laurite contains less radiogenic Os ( $^{187}\text{Os}/^{188}\text{Os} = 0.1248 \pm 0.0001$  to  $0.1250 \pm 0.0001$ ) than the composite inclusion of millerite + chalcocite that forms the core of the grain ( $^{187}\text{Os}/^{188}\text{Os} = 0.1274 \pm 0.0003$ ). Four grains of Ru–Os–Ir–Ni–Fe oxide/alloy, interpreted as derived from low-temperature desulfurisation of laurite, yield  $^{187}\text{Os}/^{188}\text{Os}$  between  $0.1210 \pm 0.0006$  and  $0.1228 \pm 0.0016$ , within the range reported for primary laurite.

González-Jiménez et al. (2013) observed that grains of laurite and base-metal minerals (including sulfides and arsenides) in chromitite and in the host peridotite of the Ojen massif (southwestern Spain) have similar values and ranges of heterogeneity in Os isotopes. Most laurites ( $n = 104$ ) and base-metal minerals ( $n = 27$ ) have  $^{187}\text{Os}/^{188}\text{Os}$  between  $0.1181 \pm 0.00003$  and  $0.1364 \pm 0.0006$ , roughly identical to the BMS of the peridotite ( $0.1159 \pm 0.0007$  to  $0.1374 \pm 0.0014$ ;  $n = 33$ ). The  $T_{\text{RD}}$  for the whole range of chromitite-hosted PGMs and BMS varies from 1.4 to  $-7.3$  Ga, whereas the peridotite-hosted phases vary between 1.71 and  $-1.32$  Ga (Fig. 4). Excluding the future ages, the  $T_{\text{RD}}$  in the chromitites clusters around a main peak at  $\sim 0.3$  with a series of minor peaks at  $\sim 0.7$ ,  $0.9$ ,  $1.0$  and  $1.4$  Ga whereas the  $T_{\text{RD}}$  in peridotite-hosted BMS clusters around three main peaks at  $\sim 0.2$ ,  $0.6$  and  $1.2$  Ga. (see Fig. 6 of González-Jiménez et al., 2013). All these model ages are much older than the age of 21 Ma estimated for the crystallisation of the chromitite using both geological and independent geochronological data.

In the strongly metamorphosed chromitites of the Dobromirski peridotite (Central Rhodope Complex, Bulgaria) laurites wholly enclosed in

unaltered chromite have  $^{187}\text{Os}/^{188}\text{Os}$  compositions from  $0.1231 \pm 0.0001$  to  $0.1270 \pm 0.0006$  ( $n = 21$ ), very distinct from the secondary laurite in the altered zones of chromitites ( $0.1124 \pm 0.0001$  to  $0.1398 \pm 0.0001$ ;  $n = 36$ ; González-Jiménez et al., 2012b). Given the low  $^{187}\text{Re}/^{188}\text{Os}$  in both populations ( $< 0.024$ ), it is probable that the wider range observed in secondary grains was produced by incorporation of variable  $^{187}\text{Os}/^{188}\text{Os}$  from fluids during metamorphism. Only grains of platinum-group minerals encased in the unaltered cores of chromite grains, far from visible fractures and alteration rims, appear to have retained pristine Os-isotope compositions that can reflect magmatic processes occurring in the mantle. Later analyses of twenty-two primary laurite grains enclosed in unaltered chromite have yielded the same range of  $^{187}\text{Os}/^{188}\text{Os}$ , except for two grains with very unradiogenic values ( $0.1097 \pm 0.0005$  and  $0.1133 \pm 0.0008$ ; Fig. 4). The  $T_{\text{RD}}$  ages of primary laurites range from 0.13 to 2.6 Ga, with a predominant clustering at 0.4 Ga. No dates are available for the formation of this “ophiolite” but two Neo-proterozoic zircons recovered from the chromitites yield Hf model ages ( $T_{\text{DM}}$ ) of 2.21 and 2.77 Ga identical to the older  $T_{\text{RD}}$  peaks for the platinum-group minerals (González-Jiménez et al., submitted for publication).

Twelve grains of laurite of Type I chromitites from Loma Baya, Guerrero State in Mexico, show  $^{187}\text{Os}/^{188}\text{Os}$  from  $0.1250 \pm 0.002$  to  $0.1271 \pm 0.0005$ , yielding  $T_{\text{RD}}$  between 0.14 and 0.45 Ga (Fig. 4).

Three chemically-zoned primary laurites hosted within unaltered chromite of the Type II chromitites of Ouen Island, New Caledonia (Fig. 4) also show significant differences in  $^{187}\text{Os}/^{188}\text{Os}$ , within the range reported for the Type I chromitites ( $0.1201 \pm 0.00008$  to  $0.1309 \pm 0.0002$ ), yielding  $T_{\text{RD}}$  between 1.1 and  $-0.39$  Ga (Fig. 4).

#### 4. Discussion

Disregarding the potential disturbance due to post-magmatic secondary processes as noted above, the distribution of the distinct platinum-group minerals in the different types of chromitites may indicate different mechanisms for the fractionation of the PGE in the chromitites.

The link, if any, between the mechanism of magmatic crystallisation of chromite, the fractionation of the PGE and the type of assemblages of platinum-group minerals that occur in the chromitites has been the subject of much debate, as indicated above. There have been two traditional main lines of thought related to crystallisation of PGM directly from melts: (1) the lattice of chromite is able to incorporate PGE at high temperatures and on cooling they are released in the form of

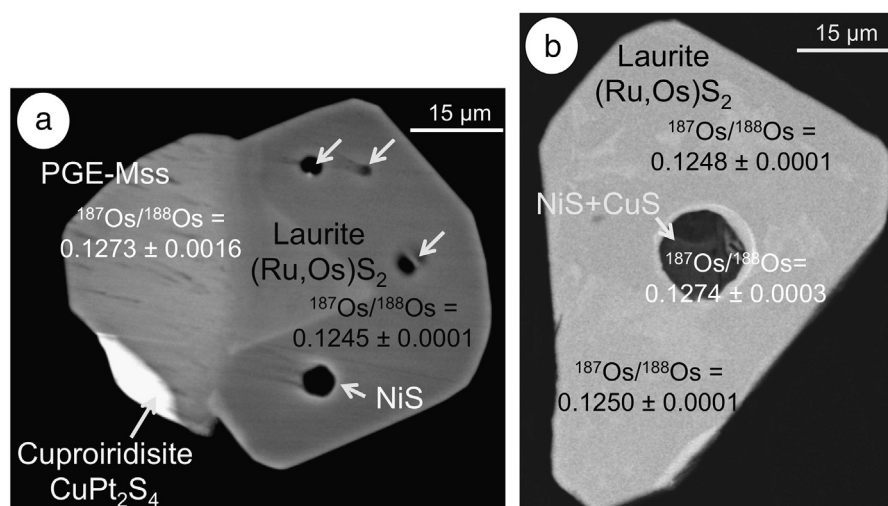


Fig. 5. Re–Os systematics of individual zoned grains of laurite associated with base-metal sulfides studied by González-Jiménez et al. (2012a) from the Caridad Mine, Mayarí-Baracoa Ophiolite, Cuba.



platinum-group minerals; (2) the platinum-group minerals have crystallised directly from fluid/melts and later were physically trapped by growing chromite crystals. However, PGMs could have also been entrained from the host rocks during melt–rock reactions associated with the formation of chromitites, deposited by fluids veining the mantle, or modified by subsolidus re-crystallisation during the travel of the chromitites in the upper mantle.

#### 4.1. Exsolution of platinum-group elements from chromite

Gijbels et al. (1974) and Naldrett and Cabri (1976) suggested that during the formation of ophiolitic chromitites PGE could fractionate into chromite at high temperatures and on cooling would exsolve from the oxide as discrete platinum-group minerals. Experimental studies indicate that Os, Ir, Ru and Rh may substitute for  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  in the chromite lattice (Capobianco, 1998; Capobianco and Drake, 1990; Capobianco et al., 1994; Richter and Downs, 2001; Richter et al., 2004) depending on temperature and  $f\text{O}_2$  (Brenan et al., 2012). Puchtel and Humayun (2001) analysed bulk-rock samples and mineral separates of komatiites and suggested that Os, Ir and Ru are compatible in chromite. However, Locmelis et al. (2011) found they could not exclude the possible presence of micro-inclusions of PGMs; they analysed chromite from S-undersaturated komatiites using in situ laser ablation ICP-MS, and showed that of all the PGEs, only Ru exists in solid solution in the crystal lattice of chromite whereas Ir occurs in the form of sub-micron Ir-bearing alloys.

Most of the experiments cited above were well outside the range of  $T$ – $f\text{O}_2$ – $P$  for the crystallisation of ophiolitic chromitites, and hence cannot be applied directly to their crystallisation. Pagé et al. (2012) analysed chromite grains from Type I chromitites by laser ablation ICP-MS, but did not detect any PGE apart from micro-inclusions of PGMs. Moreover, the visible platinum-group minerals that have been identified in chromite are randomly distributed, which is inconsistent with the more regular, crystallographically-controlled patterns expected from exsolution of PGMs within a chromite host.

The observation that individual PGMs within single chromite grains may yield distinct Os isotopic compositions even at the sub-grain scale (Fig. 5a,b) also is clearly inconsistent with the exsolution of the PGMs from the lattice of the chromite. This conclusion allows us to focus our attention on the different processes and mechanisms that might control the precipitation of PGMs from melts and fluids, and on their possible genetic connection with the chromite host.

#### 4.2. Crystallisation from melts/fluids and physical trapping by growing chromite

Augé (1985), Constantinides et al. (1980), Legendre (1982), and Stockman and Hlava (1984) suggested that the euhedral morphology and heterogeneous distribution of most platinum-group minerals in the ophiolitic chromitites reflects their direct crystallisation from melts/fluids before, or concurrently with, chromite. Tredoux et al. (1995) suggested that the enrichment of PGE in chromitites reflects the formation and physical accumulation of nano-size metal clusters of PGE (kept in suspension in the melt), which are stabilised by their adherence to chalcogenide ligands such as S, As, Sb, Te or Se. If the activity of chalcogenide elements is low, the PGE clusters will remain suspended in the silicate melt until they can coalesce to form alloys. Later work using LA-ICP-MS (Ballhaus and Sylvester, 2000; Locmelis et al., 2011; Pagé et al., 2012; Sattari et al., 2002) has confirmed the existence of such sub-micron PGE-bearing alloys, accompanying larger platinum-group minerals in the chromitites.

Experiments by Finnigan et al. (2008) and Mungall (2005) have shown that the local reduction of  $f\text{O}_2$  in the melt at the faces of growing chromite crystals, due to the preferential partitioning of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  into the oxide, may cause the saturation of the most easily oxidised PGE (Os, Ru and Ir; Amossé et al., 1990, 2000; Borisov and

Palme, 1995; Borisov and Waker, 2000; Borisov et al., 1994) and the formation of metallic “micro-nuggets” of these elements. These observations confirmed the suggestions of Tredoux et al. (1995), revealing the possible origin of the submicroscopic IPGE-alloys identified by Pagé et al. (2012).

Other experiments by Ballhaus et al. (2006), Bockrath et al. (2004a), and Matveev and Ballhaus (2002) found that during the crystallisation of chromite from a (ferropicrite) basaltic melt at 900–1400 °C and 0.4–1.5 GPa, Os–Ir–Ru alloys may form near-infinite numbers of nano-scale metallic nuggets that nucleate on the surfaces of chromite “microliths” and then coalesce into nuggets. Bockrath et al. (2004a) observed that these micro-nuggets of IPGE-alloys can be directly incorporated into growing chromite or may react with surrounding S-bearing melts to produce Ru–Os-bearing sulfides such as laurite. Their experiments also showed that Pt and Pd tend to crystallise to many fewer and much larger-sized metallic phases, most of which are suspended in the silicate glass. Rhodium behaves somewhere between these extremes, with small alloy grains attached to chromite and larger metal grains suspended freely in the glass.

The fractionation of IPGE and PPGE due to these “nugget effects” is consistent with the higher abundance of Os-, Ir-, and Ru-rich minerals enclosed in chromite, while the Pt-, Pd- and Rh-rich minerals are more concentrated along the edges of chromite grains or in the interstitial silicate matrix of the Type I chromitites (Fig. 2). It also helps to explain the higher proportion of Pt–Pd–Rh minerals in the altered zones of the chromitites (mainly edges of chromite grains and in the interstitial matrix) in the Type II chromitites (Fig. 3). In the latter, Pt–Pd–Rh minerals are still relatively abundant in unaltered chromite (37%); this may indicate their precipitation from melts that already were strongly depleted in IPGE, and were more likely to be saturated in sulfur or other chalcogenide ligands such as As, Sb or Te such as observed in some chromitites from Kraubath (Malitch et al., 2001; Thalhammer et al., 1990). This process would continue to lower temperatures, concentrating abundant PPGE in the form of sulfides in the interstitial matrix (e.g. malanite in the Ouen Island chromitites; González-Jiménez et al., 2011a).

##### 4.2.1. Crystallisation of platinum-group minerals in a dynamic regime

Experiments by Andrews and Brenan (2002), Bockrath et al. (2004a), and Brenan and Andrews (2001) showed that basaltic melt can precipitate stoichiometric laurite ( $\text{RuS}_2$ ) in equilibrium with Os–Ir alloys at 1300–1200 °C and  $\log f\text{S}_2$  from  $-2$  to  $-1.3$ . The results also show that the solubility of Os in laurite increases with decreasing  $T$  and/or increasing  $f\text{S}_2$ . Laurite from ophiolitic chromitites shows a wide range of Os contents up to the end-member erlichmanite ( $\text{OsS}_2$ ) (Garuti et al., 1999a,b; Gervilla et al., 2005; Melcher et al., 1997). Three different patterns of magmatic zoning have been observed (González-Jiménez et al., 2009b): (1) Os-poor (laurite) cores with Os-rich rims (normal zoning); (2) Os-rich cores and Os-poor rims (reverse zoning); (3) complex intergrowths of Os-rich, Os-poor laurite and erlichmanite (oscillatory zoning).

Because  $f\text{S}_2$  will increase with cooling of the melt, normal zoning in laurite–erlichmanite grains could be interpreted as recording different stages of fractional crystallisation during cooling (e.g. Augé and Johan, 1988; Augé et al., 1998; Garuti et al., 1999b; Zaccarini et al., 2004). However, this mechanism cannot explain either reverse or oscillatory patterns. To account for such chemical variations, we need a mechanism capable of creating different  $f\text{S}_2$  gradients in space and/or time, with or without changes in temperature, and over short time spans. This may have an analogue in plagioclase formed in magma chambers beneath volcanoes, in which the frequent replenishment of the magma chamber causes both thermal and chemical interactions between resident and recharge magmas, producing oscillatory zoning in the silicate (e.g. Davidson and Tepley, 1997; Shcherbakov et al., 2011).

Gervilla et al. (2005) and González-Jiménez et al. (2009b) suggested that the platinum-group minerals have crystallised within a dynamic

open system, dominated by short-term variations in  $T$ – $fO_2$ – $fS_2$  relationships. In a model proposed to explain the origin of the platinum-group minerals of Os–Ir–Ru in the Type I chromitites, they suggested that both extremely small metallic nuggets of Os, Ru and Ir (those described by Ballhaus et al., 2006 in their experiments) and submicroscopic grains (or atomic-scale clusters) of Os–Ru–(Ir) alloys (like those suggested by Tredoux et al., 1995) would nucleate in the redox boundary layers around growing chromite crystals, similar to those produced in the experiments of Finnigan et al. (2008) and Mungall (2005).

Once formed, these submicroscopic nuggets and alloys would remain attached to the surfaces of large chromite grains in equilibrium with the surrounding melt/fluid, as observed in the experiments of Ballhaus et al. (2006), Bockrath et al. (2004a), and Matveev and Ballhaus (2002). Local increases of  $T$ – $fO_2$ – $fS_2$  (and  $aAs$ ) would promote the crystallisation of laurite–erlichmanite with different Ru/(Ru + Os) ratios, Os–Ir–Ru alloys, and occasionally irarsite, at the same time but in different zones of the chromite-forming system. A dynamic environment with sudden changes of  $fS_2$  due to movement (influx) of fluids/melts within an open conduit also would explain the immiscible segregation of droplets of sulfide melts, producing the Ni–Cu–Fe sulfides that often coexist with the platinum-group minerals in chromite (see Fig. 4 in Hattori et al., 2004 and Fig. 4 in González-Jiménez et al., 2009b).

This model is supported by (1) the wide dispersion of  $^{187}Os/^{188}Os$  among individual grains of laurite (and Ni–Cu–Fe sulfides) coexisting within single grains of chromite (Ahmed et al., 2006; González-Jiménez et al., 2012a; Marchesi et al., 2011), and (2) the intra-grain Os-isotope zoning observed by González-Jiménez et al. (2012a; Fig. 5a,b). The isotopic heterogeneities might be produced by mixing of batches of basaltic melts with distinct Os-isotope compositions, derived from an already heterogeneous mantle source (Coggon, 2010; Gervilla et al., 2005; Marchesi et al., 2011 and references therein). The mixing (or mingling) of basaltic melts with contrasting physicochemical properties (i.e. different Si-contents) would generate a heterogeneous environment with variable  $T$ – $fO_2$ – $fS_2$  (and  $aAs$ ). In this scenario, minute grains of growing platinum-group minerals (and Ni–Cu–Fe sulfides) could be physically moved from one melt to another, and continued growth would produce single or composite grains with chemically and isotopically distinct compositions (Fig. 5). As noted above, this has an analogue in individual crystals of plagioclase formed in open magmatic chambers beneath volcanoes. Davidson and Tepley (1997) noted that these plagioclases may exhibit zoning in both  $\%An$  and  $^{87}Sr/^{86}Sr$  isotopes as result of a continuous replenishment of melts into the magmatic chamber, a model that applies well to the case of the chromite-hosted PGMs.

This model also may apply to Type II chromitites such as those of Ouen Island, in the New Caledonia Ophiolite (González-Jiménez et al., 2011a) in which unzoned and oscillatory-zoned laurites with significant heterogeneity in  $^{187}Os/^{188}Os$  (Fig. 4) coexist with Pt-rich alloys, and Pt ± Rh ± Ir sulfides and Ni–Cu–Fe sulfides.

The PGE budget of mantle melts precipitating chromitites is controlled both by the melting regime and the extent of reaction of PGE-carrier minerals in contact with the melt (Prichard et al., 2008 and references therein). The observations discussed above show that several generations of PGE-carrier minerals (including Ni–Cu–Fe sulfides and to a lesser extent, platinum-group alloys and sulfides), formed during multiple episodes of partial melting or metasomatism in the mantle, and commonly coexist millimetres apart in a single peridotite sample (Alard et al., 2000, 2002; Griffin et al., 2004; Marchesi et al., 2010; Xu et al., 2008). Hence, if partial melts are extracted from these domains, or migrate through them, their PGE budgets and Os-isotope compositions will tend to reflect the homogenisation of those PGE-carrier minerals. In the model discussed above, the micrometric PGMs, precipitated from multiple isotopically-distinct batches of melts (whose PGE represent several generations of peridotitic PGE-carriers), must have a PGE budget and Os-isotope composition that represents the homogenisation of several  $m^3$  of the mantle. Therefore, the

measured  $^{187}Os/^{188}Os$  of these PGMs is actually a mixture. This means that Re–Os model ages, even on individual PGE-carrier phases, may not always reflect actual episodes of melting or crystallisation in the mantle, but can provide minimum ages for such events.

#### 4.3. Assimilation of pre-existing platinum-group minerals from country host rocks?

The models described above for the crystallisation of the platinum-group minerals assume that the PGE are dissolved in the basaltic (s.l.) melts. However, Bockrath et al. (2004b) and Fonseca et al. (2012) have used experimental data to argue that in the  $P$ – $T$ – $fO_2$ – $fS_2$  region in which chromitites may form in the mantle, these silicate melts might have little ability to dissolve the PGE. Bockrath et al. (2004b) suggested that in their source region the PGE enrichment in these types of melts involves the formation of molten PGE-bearing sulfide “mattes” (sulfide partial melt forming a solid/melt mush) and their transport as entrained immiscible droplets. These molten mattes could remain entrained in the silicate melt until a decrease in pressure allows S and the PGEs to dissolve into the structure of the silicate melt. Experiments by Fonseca et al. (2012) and Peregoedova et al. (2004) produced analogous PGE-bearing sulfide mattes. The latter authors argued that during a continuous extraction of partial melts from the mantle, the concentration of S and FeO into these melts may promote the desulfurization of the sulfide matte and the formation of discrete PGMs, especially Os- and Ir-bearing alloys.

As Re/Os in sulfides is very sensitive to the degree of melting, the formation of residual Os–Ir alloys by the breakdown of sulfides can be directly linked with the interpretation that Re-depletion model ages of the alloys reflect a *true* event of depletion in the mantle (Fonseca et al., 2012). In this scenario, the formation of the platinum-group minerals may reflect different events of: (1) extraction of the parental melts of the chromitites from their peridotitic source; (2) timing of melt–rock reactions, involving destruction of PGE-bearing sulfides, that take place during upward migration/emplacement of these melts in the mantle.

A series of small events of melt extraction and melt–rock reaction may produce a progressive but stepped sequence of decreasing  $fS_2$  in the mantle source region, promoting the breakdown of PGE-bearing base-metal sulfides into “residual” laurites, and to a major extent Os–Ir alloys, thus explaining the broad coincidence of the  $T_{RD}$  ages of many platinum-group minerals with known magmatic events related to ophiolite formation. For example Group II Os–Ir alloys of Tibetan chromitites, interpreted by Shi et al. (2007) as produced through the breakdown of sulfides, yield  $T_{RD}$  model ages that coincide broadly with the timing of known crust-formation events. This mechanism could also help to explain the old “residual” laurites associated with larger Ni–Fe–Cu sulfides in some mantle peridotites (e.g. in Lherz; Lorand et al., 2010).

During the processes of melt–rock reaction and melt transport and pooling associated with the formation of the chromitites these *residual* Os–Ir alloys can be transported as sub-microscopic or larger grains in water- and volatile-rich melts at high temperature and low pressure and low  $fS_2$ , thus preserving the  $^{187}Os/^{188}Os$  of the mantle source. Some of these alloys could also react with S promoting the formation of laurite (Bockrath et al., 2004a; Grieco et al., 2006), thus explaining why in the Ojén massif, chromite-hosted PGMs and base-metal minerals and peridotite-hosted BMS sulfides have similar ranges of  $^{187}Os/^{188}Os$  (González-Jiménez et al., 2013).

However, not all platinum-group minerals now hosted in ophiolitic chromitites were necessarily formed by direct precipitation from melts or released from sulfide mattes. Some of them could be physically entrained from the host rocks by the parental melt during melt–rock reactions associated with their ascent through the mantle, thus contributing to their budget of platinum-group elements and explaining the variable scales of Os-isotope heterogeneity in the platinum-group



minerals. Several studies have documented platinum-group minerals of both residual and metasomatic origin in mantle peridotites. [Luguet et al. \(2007\)](#) identified residual platinum-group alloys in depleted abyssal peridotites from the Kane Fracture Zone. Similarly, [Lorand et al. \(2010\)](#) detected residual laurite–erlichmanite and abundant grains of Pt–Ir–Os alloy (up to 3 µm across) inherited from an ancient highly-depleted harzburgite protolith in the refertilised Iherzolitic rocks of the Lherz Massif. They also identified “low-temperature” Pt- and Pd-rich bismuthotellurides and arsenides/sulfarsenides associated with metasomatic BMS. [Hutchinson et al. \(1999\)](#) found metasomatic PGMs associated with sulfides in poikilitic clinopyroxene-rich patches in the mantle harzburgite of the Troodos ophiolites in Cyprus.

#### 4.4. Mantle veining?

The study of peridotites in both exposed ultramafic massifs and peridotite mantle xenoliths has shown that the triggering of crack propagation in the mantle due to fluid overpressure may provide a robust pathway for the transport of metasomatic fluids and melts over significant distances ([O'Reilly and Griffin, 2010, 2012](#); references therein). Evidence for crack-filling fluids comes from the ubiquitous planar arrays of sulfide- and fluid inclusions within mineral grains in xenoliths, interpreted as healed fractures originally filled with melt/fluids. The common euhedral to subhedral forms of such inclusions are interpreted as negative-crystal habits imposed as the host grain recrystallised to reduce the surface free energy of the grain ([Roedder, 1984](#)).

Linear arrays or trails consisting of base-metal minerals ± silicates ± fluid/melt inclusions have been described in both unaltered and altered zones of chromite grains in ophiolitic chromitites ([Melcher et al., 1997](#); [Whittaker, 1983](#); [Whittaker and Watkinson, 1984](#)). [Melcher et al. \(1997\)](#) observed that some of these arrays contained serpentine and chlorite and interpreted them as formed during metamorphism or serpentinisation, and then enclosed by recrystallising chromite during grain-boundary migration. [Whittaker \(1983\)](#) observed that some of those trails or planar arrays contained base-metal sulfides associated with silicate and fluid/melt inclusions of only primary origin. They interpreted these as produced by fluid migration along a fracture or break in chromite which has since healed, similar to those seen in xenoliths. [Fig. 1-4](#) shows a trail of laurite grains within an unaltered grain of chromite. All these observations suggest that in the chromitites we can find two generations of inclusion trails; an early one formed at high temperature by magmatic processes in the mantle and a second one formed during serpentinisation or metamorphism. However, the low-temperature re-equilibration of high-T magmatic inclusions to give the later ones cannot be ruled out. Both types of arrays may coexist within unaltered chromite grains.

The formation of “primary” fluid-filled fractures in the chromitites could take place by crack propagation due to fluid overpressure, or by brittle deformation in the shallow mantle ([Kirby et al., 1987](#); [Maaløe, 2003](#); [O'Reilly and Griffin, 2010, 2012](#)). Plastic deformation in the upper mantle commonly develops instantaneous tension fracturing in massive chromitites ([Leblanc and Nicolas, 1992](#)), analogous to those documented in mantle peridotites, allowing fluid infiltration by crack propagation. In upper mantle the temperature is relatively high for long periods of times, allowing such fractures to anneal. The relics of this process are now solid inclusions (e.g., PGM or base metal minerals; [Fig. 1-4](#)) ± silicates ± fluid/melt that are most commonly arranged in linear trails or planar swarm. Nevertheless, some of these structures might be also marked on the scale of a hand-sample by veinlets of silicates (primary or secondary), a few millimetres in thickness, and on the deposit scale by veins of dunite perpendicular to the major axis of the chromitite body, such as observed by [Leblanc and Nicolas \(1992\)](#).

An excellent example of the process described by [Leblanc and Nicolas \(1992\)](#), but involving the precipitation of PGMs is found in

the chromitites of Loma Baya in Mexico ([Fig. 1-8](#)). In these chromitites, “secondary” veins of chlorite cut pre-existing fractures in chromite grains and host unaltered laurite with euhedral shapes (e.g. [Fig. 1-8](#)) and similar compositions to those enclosed in unaltered chromite grains. The crosscutting nature of the chlorite veins in the Loma Baya case clearly indicates that the melt/fluid that precipitated the PGM and its host silicate was introduced into already solid chromite. In ophiolitic chromitites, laurite in contact with chlorite is usually altered and the common interpretation is that laurite had crystallised with a magmatic *postcumulus* silicate, both being altered during post-magmatic processes (e.g. [Ghorfi et al., 2008](#); [Tarkian and Prichard, 1987](#); [Zaccarini et al., 2005, 2010](#)). According to this hypothesis the features of the Loma Baya laurite in the chlorite vein can be interpreted to show that it was “somehow preserved” from alteration, or more likely that it precipitated from the same fluid that deposited chlorite. This would be evidence that the temperature of equilibration of laurite in hydrous fluids could be much lower than has been estimated in experiments on dry basaltic melts (~1200 °C; [Andrews and Brenan, 2002](#); [Bockrath et al., 2004a](#); [Brenan and Andrews, 2001](#)).

#### 4.5. Subsidiary recrystallisation?

[Gervilla et al. \(2012\)](#) showed that at 700–550 °C (depending on pressure) the infiltration of water into chromitites might promote the reaction of primary chromite with olivine from the matrix to produce chlorite in equilibrium with “secondary” chromite residually enriched in Cr and Fe<sup>2+</sup> (ferrous chromite). According to these authors, this reaction produces ~43% loss of the mass of chromite that is compensated not by modification of the initial size of the chromite grain but by the development of a spongy or porous texture in the ferrous chromite. They also observed that some pores remain empty; such pores are unlikely to remain open unless this occurs at the surface – so the open pores may originally have been fluid-filled. However, most of them now are filled by chlorite produced as a consequence of this reaction.

The interconnected network of pores associated with the formation of the spongy or porous texture (with fluid-filled pores) makes the circulation of fluids easier, favouring the reaction of the magmatic PGMs with the hydrothermal fluids. As the formation of porous ferrous chromite takes places under reducing conditions ([Gervilla et al., 2012](#)) it is expected that magmatic sulfides would be destabilised via desulfurisation, consistent with the S-deficiency shown by many laurites found in the porous rims of metamorphosed chromitites (e.g. [González-Jiménez et al., 2010, 2012b](#); [Prichard and Tarkian, 1988](#); [Thalhammer et al., 1990](#); [Yang and Seccombe, 1993](#)). However, in some other metamorphosed chromitites, laurite sited in porous chromite overgrows clusters of secondary Ru–Os–Ir alloys or irarsite ([Fig. 1-10](#), and see also [Fig. 6b](#) in [González-Jiménez et al., 2010](#)); this suggests that the laurite might also recrystallise at relatively low temperature. It is plausible that Ru–Os–Ir metal nuggets formed by desulfurisation of magmatic laurite–erlichmanite remained within chromite pores and reacted later with S-bearing solutions to produce an overgrowth of “secondary” laurite. This mechanism of dissolution–precipitation could explain why some metamorphosed chromitites have laurite associated with chlorite (or laurite with chlorite inclusions; [Fig. 1-9](#)), commonly filling cavities in porous chromite ([Fig. 1-11](#)).

An example that may reflect an almost complete sequence of this process is preserved in the metamorphosed chromitites studied by [Proenza et al. \(2008\)](#) in the Argentinian Pampean Ranges (see [Fig. 9b–c](#) in that paper). In this case, two small grains of erlichmanite fill former pores in altered chromite, which encloses a large crystal of chlorite replaced by serpentine. The serpentine grain hosts two zoned laurite grains with Os-rich cores and Ru-rich rims, which in turn are mantled by Ru oxide/hydroxide containing inclusions of metallic Pt and irarsite. Although it is difficult to establish the complete sequence

of alteration, it is plausible that during the initial stage of metamorphic alteration of chromite to porous chromite and chlorite, the magmatic laurite was liberated to the matrix, altered and reworked, freeing up some Os (leaving Ru-rich rims on the laurite and an external Ru oxide/hydroxide). The liberated Os (and probably S) would be fixed within a short distance, contributing to the formation of erlichmanite in pores of the altered chromite, which were sealed during the formation of the new chromite–ferrian chromite grain boundary.

Interestingly, laurites found in the porous chromite rims of the metamorphosed chromitites of Dobromirski show a wider dispersion of  $^{187}\text{Os}/^{188}\text{Os}$  than laurites enclosed in fresh chromite (González-Jiménez et al., 2012b), suggesting that hydrothermal fluids reacting with Os-bearing PGMs are able to remobilise the Os and disturb the original Os-isotope compositions. This mechanism is analogous to the modification of the Os-isotope signatures in mantle sulfides when they react with migrating metasomatic melts (Griffin et al., 2004).

However, if these secondary laurites were formed by resulfurisation of secondary Ru–Os–Ir alloys, why some of them are euhedral, (e.g. Fig. 1–10) like magmatic laurites? Thermodynamic and chemical modelling by Gervilla et al. (2012) predicts that the reaction that causes the alteration of chromite is reversible. Thus, if a grain of altered chromite is heated enough, it can recrystallise as a new homogenous chromite with the same composition as the original chromite. It can be expected that during its crystallisation this newly-formed chromite will impose a negative euhedral shape on the “secondary” PGM, which is also recrystallising, thus producing the polygonal boundaries of the secondary PGMs observed in the progressively metamorphosed chromitites of Loma Baya (Fig. 1–10). If the temperature increases sufficiently, it could also eventually produce the complete homogenisation of the newly-formed PGM, eliminating the record of its previous history of alteration. Therefore, in completely recrystallised chromites with homogenous textures, the “euhedral” and “homogenised” newly-formed PGM may be indistinguishable from the original euhedral magmatic platinum-group minerals – at least in terms of their microstructures and major-element compositions.

This hypothesis is an alternative explanation of why many chromites, with homogenous textures and compositions similar to primary chromite, contain polyphase inclusions made up of platinum-group minerals together with chlorite (or serpentine). We suggest that such inclusions could not be primary silicates re-equilibrated during sub-solidus cooling as in the traditional interpretation (Proenza et al., 2008). Instead, they probably are relics of the post-magmatic alteration of chromite, which were trapped with the secondary “newly-formed” platinum-group minerals when the grain boundaries of the recrystallising chromite migrated during metamorphism (Gervilla et al., 2012). Multiple cycles of alteration/re-equilibration of the chromitites might have produced several events of dissolution–precipitation–homogenisation of grains of PGMs, which we expect to produce disturbance of  $^{187}\text{Os}/^{188}\text{Os}$ . This effect may produce both a spread in  $^{187}\text{Os}/^{188}\text{Os}$  values, as observed González-Jiménez et al. (2012b) in Dobromirski, or homogenization as may have occurred in the UHP chromitites of Luobusa (Fig. 4). This uncertainty highlights the necessity of additional studies to better constrain this process.

According to this concept, part of the variability that now is observed in the platinum-group minerals that we have interpreted as “primary” could be produced when chromitites were exhumed and altered at shallow levels in the upper mantle, then later buried again to re-equilibrate at higher temperature and pressure. Such recycling (Arai, 2010) would contribute to the formation of multiple generations of “newly-formed” PGMs. In the “re-equilibrated” (metamorphosed) chromitites these PGMs could be found within homogenous chromite grains, giving the appearance of magmatic PGMs.

## 5. Conclusions and pending problems

- (1) Numerous studies have reported the occurrence of platinum-group minerals in ophiolitic chromitites in three main

microstructural positions: in chromite, in fractures and in the interstitial silicate matrix. Our observations suggest a more complex distribution with grains found in (1) *unaltered cores of chromite* (usually interpreted as magmatic), (2) *altered inner zones or edges of chromite grains* made up of ferrous and/or ferrian chromite exhibiting both homogenous or porous textures, (3) *open fractures* that may have irregular outlines and/or alteration rims and/or be filled by secondary silicates, and (4) *inclusion trails* in both unaltered or altered zones within chromite grains.

- (2) The distribution of the platinum-group minerals in the different types of chromitites is consistent with their abundance of the PGE in whole-rock analyses. Type I chromitites are enriched in Os–Ir–Ru-rich minerals whereas Type II have predominantly Pt–Pd–Rh-rich minerals. Approximately 92% of the PGMs found in the unaltered chromite grains of Type I chromitites are Os–Ir–Ru minerals.
- (3) The in situ analysis of the Os isotopes in individual grains of platinum-group minerals of ophiolitic chromitites reveals very heterogeneous compositions, even at the scale of single micrometric grains. In some ophiolitic chromitites the platinum-group minerals found in a single chromite deposit (or even single chromite grain) may show a spectrum of rhenium-depletion model ages from  $>2$  Ga to  $<0$  Ga (future ages).
- (4) The integrated analysis of the microstructural position of platinum-group minerals in the chromitites and their in situ Os-isotope compositions rules out an origin by solution of PGE in chromite at high temperature and their later exsolution as discrete PGMs. The genesis of PGMs with heterogeneous Os-isotope compositions probably reflects the crystallisation of chromite by the mixing/mingling of multiple batches of melts that have sampled different mantle sources. This mixing mechanism may produce “mixed” Os-isotope compositions even within single PGM: their  $T_{\text{RD}}$  may not reflect the timing of real episodes of melting or crystallisation in the mantle, but may provide minimum ages.
- (5) Three new mechanisms have been proposed to explain the features/origins of platinum-group minerals in ophiolitic chromitites. The first mechanism suggests that not all PGMs now hosted in the ophiolitic chromitites were necessarily formed by direct precipitation from melts. Residual phases such as laurite or Os–Ir alloys could be produced by the breakdown of pre-existing PGE-bearing base-metal sulfides in the mantle, liberated during melt–rock reaction as sulfide mattes. Platinum-group minerals already present in the mantle peridotite also could be incorporated as a solid or a solid/melt mush into the parental melts of chromitites. The second mechanism suggests that the platinum-group minerals were introduced into pre-existing chromitites once they were formed. Chromitites may be transported deep into the mantle by subduction processes, and possibly integrated into the convecting mantle. They can be infiltrated and veined by metasomatic fluids/melts that would promote the precipitation of platinum-group minerals. The third mechanism involves the partial or complete destruction of the PGMs, and their recrystallisation, during polyphase metamorphism or recycling of the chromitites in the deeper mantle.
- (6) The contribution of these three mechanisms: assimilation of pre-existing PGMs from the host rock; mantle veining; and subsolidus recrystallisation, to the budget of PGMs (and BMS) in the chromitites warrants future studies. It is obvious that incorporation of pre-existing platinum-group minerals from peridotites cannot explain the abundance of platinum-group minerals in the chromitites. However, the actual abundance of micrometric PGMs in the country-rock peridotites hosting chromitites has been overlooked; their contribution to the PGE (and Os-isotope) budgets and their petrogenetic significance have not been examined. This also warrants future study, particularly to understand the ancient ( $>1$  Ga)  $T_{\text{RD}}$  model

ages observed in some chromitite-hosted PGMs from Phanerozoic ophiolites (Fig. 4). The future of this research will be facilitated by new techniques of hydrosynthesis, which have demonstrated success in recovering numerous tiny PGMs from low-PGE samples where these types of minerals were initially not detected in situ nor recovered by conventional separation techniques. On the other hand, future studies of trace elements in the chromite and the PGMs, combined with microstructural (electron back-scatter diffraction (EBSD)) studies of the distribution of the PGMs in chromite, will help to evaluate the hypothesis for the origin of the PGMs as produced by mantle veining and subsolidus recrystallisation. Improved identification of PGM crystallised from the same melts that produced the chromites as well as “pre-existing” and “post-formation of the chromitite” in our dataset will help us understand the history of chromitites in the upper mantle.

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