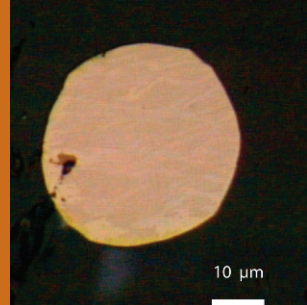


# Platinum-Group Elements: A New Set of Key Tracers for the Earth's Interior

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Monosulfide solid solution included in a mantle olivine. Plane-polarized reflected light

**Due to their “iron-loving” properties, platinum-group elements (PGE) are expected to be stored in the Earth’s core. Although very low, at a few parts per billion, PGE concentrations measured in mantle-derived rocks are too high to be in chemical equilibrium with the core. The “late veneer” model offers the best explanation for this paradox—it postulates that a flux of primitive meteorites hit the early Earth after core formation had ceased. However, the inferred PGE composition of the hypothetical primitive mantle exhibits slight positive excesses of Ru, Rh, and Pd compared to the canonical chondritic signature. Such deviations have triggered considerable debate about the composition of the late veneer and the extent of reworking of PGE signatures by igneous processes within the Earth’s mantle.**

KEYWORDS: platinum-group elements, core, upper mantle, chondrites, base-metal sulfides

## INTRODUCTION

Thanks to advances in analytical chemistry and low-detection multielement analytical facilities, platinum-group elements (PGE) recently joined the panel of geochemical tracers of the Earth’s mantle, thirty years after the rare earth elements (REE) and other lithophile elements that are concentrated in silicates and oxides. In the periodic table of the elements, the PGE are classified, along with Fe, Ni, and Co, as Group VIII transition metals. As transition metals, they possess unfilled high-energy electronic d-orbitals containing unpaired electrons that may be engaged in metal–metal bonding or covalent bonding with electron acceptors like sulfur. Thus PGE display a strong affinity for metallic phases and sulfides, which results in very different properties during planetary differentiation compared to lithophile elements. As such they provide unique clues about processes related to the origin of the terrestrial planets, processes such as core segregation and continuous accretion from primitive meteorites. Recent work has shown that PGE also offer new and complementary perspectives on the relations between the lithophile elements and the geodynamic evolution of the Earth’s mantle and on igneous processes such as melting and magma–rock interaction. However, since most of the PGE information is carried in minerals (sulfides, alloys) representing less than 0.1% by volume of

the Earth’s mantle, understanding the PGE abundance in the mantle requires “sharp” analytical tools and new conceptual frameworks that will allow us to extrapolate from the behavior of trace minerals to evolution at the planetary scale.

## PGE BUDGET OF THE EARTH

The Earth is a differentiated planet with a metallic core (ca. 33% of the Earth’s mass) surrounded by a silicate shell consisting of the mantle (66.4% by weight) and a thin (30–50 km) crust (0.4% by weight). It is generally accepted that the Earth grew by the accretion of a few

tens of protoplanets (bodies up to thousands of kilometers in diameter) within  $10^7$  to  $10^8$  years after the formation of the solar system. Due to their high ( $>10^4$ ) metal–silicate partition coefficients ( $D^{\text{met/sil}}$ , i.e. the concentration of a given element in an Fe–Ni metal alloy divided by the concentration of the same element in molten silicate), it is widely believed that the PGE delivered to the proto-Earth at the accretionary stage were massively sequestered into the metallic core during the core–mantle separation event, more than 4.5 billion years ago. However, as the core cannot be probed directly, information on its composition must be gleaned indirectly by (1) using  $D^{\text{met/sil}}$  for the PGE measured in the laboratory, (2) using the respective masses of the core and mantle, and (3) assuming that chondritic meteorites are the best proxies for the cosmic materials that built up the Earth. A calculation using a conservative  $D^{\text{met/sil}}$  value of  $10^4$  for the PGE shows that more than 99.8% of the PGE were sequestered into the Earth’s core, which is expected to contain ca. 1–3 ppm Os–Ir, 2.2–4.2 ppm Ru, 3.3–5.5 ppm Pt, 1.7–3.15 ppm Pd, and 0.4–0.8 ppm Rh. It can be easily inferred from the mass-balance calculation discussed above that the silicate Earth immediately after core formation was almost completely stripped of PGE.

Unlike the core, the mantle can be sampled directly by peridotites (see page 250) and indirectly by lavas. Both indicate PGE concentrations at levels of a few parts per billion (ppb), two orders of magnitude lower than in chondritic meteorites. Nevertheless, absolute abundances are too high (by several orders of magnitude) and relative abundances too close to ratios measured in chondritic meteorites to be inherited from the core-segregation event. Indeed,  $D^{\text{met/sil}}$  for the PGE are so extremely variable, spanning several orders of magnitude, that for instance the Pd/Ir and Ru/Pt ratios of the silicate Earth should be about 100 times higher than the chondritic ratios (Fig. 1). To account for the near-chondritic relative abundances of the PGE—one of the most elusive

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geochemical aspects of the Earth's mantle—the most popular (but still not universally accepted) model assumes a continuous influx of chondritic materials (the “late veneer” model; Chou 1978) after the Earth had already acquired about 99% of its present mass and core formation was completed. This late extraterrestrial influx (ca.  $10^{22}$  kg) was thoroughly mixed within the silicate Earth but failed to segregate into the core. The Moon has preserved physical evidence of a “late heavy bombardment” (LHB; 4.0–3.8 Ga) that produced large impact basins (lunar maria) (Koeberl 2006). It is widely conjectured that the Earth suffered an LHB at the same time as the Moon. Unfortunately, there is no indisputable record on Earth, because the pre-3.8 Ga crust has been almost completely reprocessed by vigorous geodynamic activity.

Recently, several workers have explored experimentally the possibility that the comparatively high abundances of PGE in the mantle are a result of increasing solubility of these elements in silicate melts at high pressure (Fig. 1). The proponents of this model assume (1) a partially molten proto-Earth and (2) that core-forming metals were able to sink through a magma ocean extending to depths of 800–1800 km, reaching equilibrium with silicate melt at high temperature and high pressure (Righter 2003). Mantle abundances of some transition elements (Ni, Co, Mo, W) showing less affinity for Fe than the PGE have been successfully explained this way (Wade and Wood 2005). The general question of PGE solubility at high pressure remains unresolved, notwithstanding the success of Righter et al. (2007) in approaching the Pd mantle abundance by metal–silicate partitioning at the pressure conditions reigning at a depth of ca. 800 km (Fig. 1). For the same depth, Cottrell and Walker (2006) and Ertel et al. (2006) estimated contrasting  $D^{\text{met/sil}}$  values for Pt, differing by 6 orders of magnitude. To account for chondritic PGE ratios, the metal–silicate partition coefficient of each PGE must converge to the same value for the appropriate pressure range of core formation; this assumption is highly unlikely owing to the vastly different low-temperature geochemical

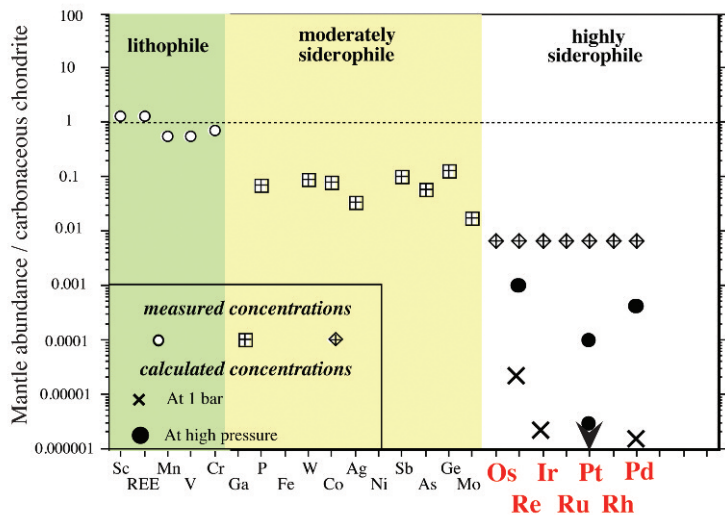
behaviors of the different PGE. In addition to chondritic PGE ratios, the model composition of the Earth's primitive mantle yields a chondritic Re/Os ratio (Meisel et al. 2001). Such a ratio likely would not have survived metal–silicate partitioning at high pressure because Re, another iron-loving element, has a much lower affinity for metal than Os.

## PARTIAL MELTING AND PGE MICRO-MINERALS IN THE TERRESTRIAL MANTLE

Most geodynamicists argue that large parts of the modern mantle have been processed via convection and plate tectonics for the last 3 billion years. Upwelling mantle columns at divergent plate boundaries melt partially, generating magmas enriched in incompatible elements and leaving behind solid mantle residues in which compatible elements are concentrated. Mantle melting is the most important Earth process that fractionates PGE and therefore must be addressed before discussing PGE signatures inherited from the primitive mantle.

If plotted in order of decreasing melting temperature for the pure metal, PGE abundances in magmas produce positively sloped patterns, while restitic mantle rocks show smooth negative slopes (Fig. 2). PGE are unlikely to exist as pure metals in the convecting mantle; thus, the question of which minerals sequester Os, Ir, Ru, and Rh in the mantle—and therefore control their compatible behavior—has been debated for more than 30 years. Olivine and Cr spinel, the two principal minerals that are refractory to mantle melting, are good candidates from a theoretical crystal-chemical point of view. Small divalent Os and Ir ions (0.74 Å) could substitute for base metals in regular octahedral sites in olivine (Brenan et al. 2005), whereas Cr spinel can accommodate Ir, Ru, and Rh substituting for trivalent cations (Capobianco and Drake 1990; Righter et al. 2004). The analysis of PGE in mantle silicates is extremely difficult because concentrations are close to the analytical detection limit and prone to contamination by PGE-rich micro-nuggets, especially in the case of opaque minerals such as Cr spinel. PGE contents ranging between 0.03 and 0.1 ppb have been measured in mantle olivine. Since olivine is the main silicate in the upper mantle (55–90% by volume), less than 10% of the whole-rock PGE budget is believed to reside in silicates (Handler and Bennett 1999; Burton et al. 2002). This percentage does not increase significantly in olivine-rich restitic rocks produced by the loss of 25% of basaltic magma via partial melting (Luguet et al. 2007). Cr spinel may concentrate Ir, Ru, and Rh at tens of ppb levels; however, Cr spinel is present in such small amounts in mantle rocks (<2–3% by volume) that its contribution is negligible.

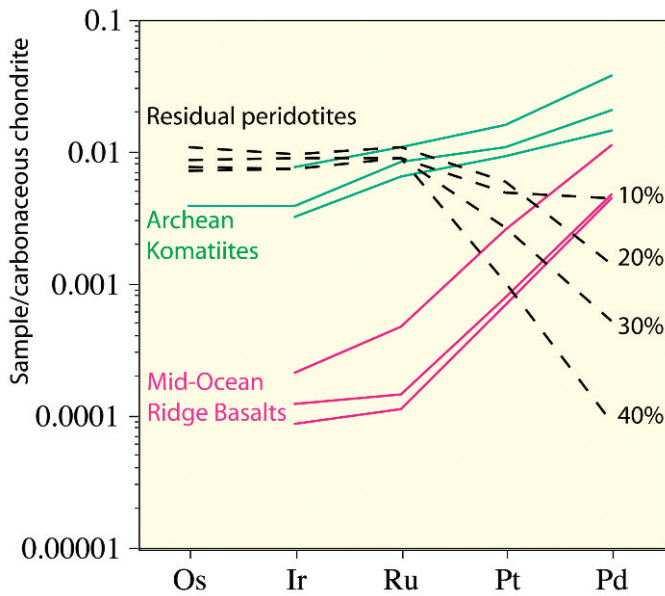
In addition to major silicate and oxide minerals, the upper mantle typically contains about 0.1 vol% of Fe–Ni–Cu sulfides (“base-metal sulfides”). The PGE concentrations measured in base-metal sulfides are at the ppm level, three orders of magnitude higher than those measured in bulk-rock powders of mantle-derived rocks (Morgan 1986; Pattou et al. 1996; Burton et al. 2002). Thus, base-metal sulfides play a pivotal role in controlling PGE abundances in mantle-derived magmas (see Mungall and Naldrett 2008 this issue). Since PGE have an extremely strong affinity for sulfides (sulfide melt–silicate melt partition coefficients of  $10^3$ – $10^6$ ; Ballhaus et al. 2006), magmas in equilibrium with sulfides remaining in the residual mantle (like basalts erupted at ocean spreading centers—MORB; Fig. 2) are PGE poor (Bézos et al. 2005). Magmas formed by a high degree of partial melting, i.e. beyond complete consumption of sulfides, (like Archean komatiites) are PGE rich, their PGE concentrations approaching primitive mantle values (Puchtel et al. 2004; Fig. 2).



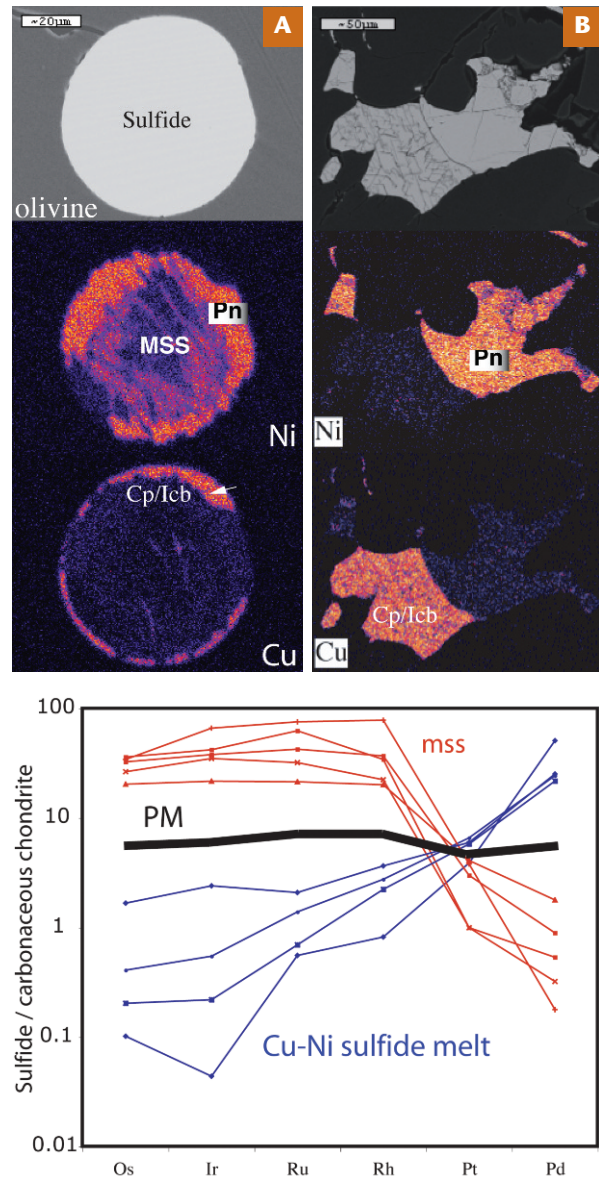
**FIGURE 1** Elemental mantle abundances relative to carbonaceous chondrite. The stair-step depletion pattern is a function of the affinity of each group of elements for iron; thus, lithophile elements, which have no affinity for iron, occur at the chondrite concentration level in the terrestrial mantle, whereas the PGE, Re, and Au, which are “iron-loving elements,” are depleted by two orders of magnitude relative to chondritic meteorites. The uniform depletion of these highly siderophile elements cannot be modelled by metallic melt–silicate melt partition coefficients determined at 1 bar pressure. The use of high-pressure metallic melt–silicate melt partition coefficients can reconcile the abundance of Pd (Righter et al. 2007) but not that of Pt (Ertel et al. 2006). FIGURE ADAPTED FROM DRAKE AND RIGHTER (2002) AND COTTRELL AND WALKER (2006)

However, the model above is unable to explain the fractionated chondrite-normalized PGE patterns that characterize residual mantle rocks and mantle-derived magmas as a whole, because experimental data show that all PGE display equal affinity for sulfide melts (Ballhaus et al. 2006). A possible solution to this conundrum was recently provided by comprehensive mineralogical investigations of PGE mineral carriers in peridotites and by laboratory experiments. In the late 1990s, a major breakthrough resulted from advances in microanalytical tools (especially laser-based microprobes coupled with plasma mass spectrometers). These techniques allowed base-metal sulfides to be analyzed in situ in polished sections, thus eliminating the tedious step of hand picking scarce and tiny (<0.1 mm) minerals, while preserving information on the sulfide minerals to be analyzed, such as their parageneses and their textural relations with respect to mantle silicates and oxides. In situ analyses confirmed conclusions based on previous analyses of separated sulfides, i.e. that more than 90% of the PGE budget of mantle lherzolite resides in base-metal sulfides (Alard et al. 2000; Lorand and Alard 2001). Moreover, Alard et al. (2000) identified two sulfide populations in mantle lherzolite, occupying different sites of crystallization and showing contrasting mineralogical and geochemical compositions (Fig. 3). They found Os–Ir–Ru- and Rh-rich sulfides in the form of rounded Fe–Ni monosulfide solid solution (mss) inclusions in olivine, and these sulfides display the same negatively sloped chondrite-normalized PGE pattern as residual (depleted) mantle peridotites. Palladium is enriched in the second population, consisting of intergranular Ni sulfide

(pentlandite) and Cu sulfide (chalcopyrite–isocubanite), which are the crystallization products of a Cu–Ni-rich sulfide melt with a basalt-like, positively sloped chondrite-normalized PGE pattern. During partial melting, the Pd- and Pt-rich Cu–Ni-sulfide melt is entrained in mantle-derived magmas, whereas mss is trapped in restitic rocks, thus sequestering Os, Ir, Ru, and Rh and producing the typical negatively sloped pattern of the residual mantle (Ballhaus et al. 2006). However, because a silicate melt dissolves thousands of ppm of sulfur, all the mss is expected to be consumed by the magma if the degree of partial melting is sufficiently high (currently estimated at  $\geq 20 \pm 5\%$ ). At this stage, the mss liberates micrometer-scale Ru–Os–Ir sulfides/ alloys and Pt–Ir alloys, which retain the PGE inside the residual peridotite (Luguet et al. 2007).



**FIGURE 2** Chondrite-normalized PGE abundances in residual mantle rocks (dashed lines) and mantle-derived magmas (colored lines). Due to extraction of the low-melting-temperature Cu–Ni-sulfide melt, which concentrates Pt and Pd, the PGE patterns of residual mantle rocks are depleted in Pt and Pd. The depletion factor increases with the degree of melting (10 to 40%), and therefore with the amount of magma extracted from the mantle column, due to the concentration of the PGE in monosulfide solid solution (mss) and to the fact that an increase in the degree of melting decreases the amount of mss remaining in the residual mantle. DATA SOURCES: HANDLER AND BENNETT 1999; PEARSON ET AL. 2004; LUGUET ET AL. 2007). Mantle-derived magmas show the opposite behavior: mid-ocean ridge basalts are IPGE-depleted (IPGE = Ir, Os, Ru) relative to the mantle composition because their mantle source still contains base-metal sulfides. In contrast, the very high (30–50%) degree of partial melting needed to generate Archean komatiitic magma, a now-extinct type of highly magnesian magma, consumed all the base-metal sulfides in the mantle, generating PGE abundances (absolute and relative) close to those of the mantle. DATA SOURCES FOR ARCHEAN KOMATIITES: REHKÄMPER ET AL. (1999b); PUCHTEL ET AL. (2004); AND FOR MORB: REHKÄMPER ET AL. (1999b); BEZOS ET AL. (2005)



**FIGURE 3** Backscattered-electron images, elemental (Ni and Cu) X-ray maps, and in situ analyses of the two populations of base-metal sulfides from mantle-derived rocks. (A) “Residual” Fe–Ni-monosulfide inclusion in olivine. (B) “Basaltic” intergranular sulfide bleb. The color intensity indicates the relative abundance of the element. Mss: monosulfide solid solution; Pn: pentlandite; Cp/Icb: chalcopyrite–isocubanite. The chondrite-normalized PGE patterns are from a combination of different peridotites. Note that a combination of “residual” mss and an appropriate amount of “basaltic” intergranular sulfide produces a primitive mantle (PM)-like PGE pattern. DATA SOURCES: ALARD ET AL. (2000); LORAND AND ALARD (2001)

## THE PGE COMPOSITION OF THE EARTH'S PRIMITIVE MANTLE

PGE in mantle rocks can potentially be used to fingerprint the characteristics of meteorites that hit the primitive Earth during late accretion. The analyses of chondritic meteorites, periodically refined over the past twenty years, indicate differences in absolute PGE abundances among the meteorites, in addition to fractionation between the refractory (Os, Ir, Ru) and the more volatile (Pd) elements (see Fig. 5 in Palme 2008 this issue). Determining the composition of the late veneer is of prime importance for the early history of the Earth, and it has even been suggested that this event delivered the water and organic molecules that were the precursors of life (Drake and Righter 2002). The degree to which PGE signatures of modern mantle rocks provide information on the early Earth depends primarily on primitive mantle (PM, also referred to as “primitive upper mantle”; Meisel et al. 2001) compositional estimates, the hypothetical model composition for the silicate Earth before any mantle-crust differentiation and mantle-melting event. Of course, the PM cannot be directly determined from mantle-derived samples. Its composition is based on extrapolations from geochemical trends shown by mantle samples, considering chondrites as the building blocks of the Earth (McDonough and Sun 1995). To characterize the PGE content of the Earth's primitive mantle, geochemists analyze lherzolites, i.e. peridotites that have major-element compositions approaching model compositions for the Earth's PM. Lherzolites are brought up from the Earth's interior to the surface as centimeter- to decimeter-sized nodules (mantle xenoliths) included in continental lavas or, less commonly, as kilometer-sized bodies tectonically uplifted through the lithosphere along major faults in Phanerozoic mountain belts (Fig. 4). Until the mid-1990s, PGE were difficult to analyze at mantle concentration levels with an acceptable degree of confidence. Pioneering measurements were accomplished for Ir and Pd, two elements easily detected by radioactivation analysis of rock powders, and the abundances of the other PGE were extrapolated from PGE ratios in carbonaceous chondrites, which are the most primitive meteorites and which are rich in volatile components and organic matter (McDonough and Sun 1995).

Compositional data for PGE in the Earth's mantle have accumulated over the past ten years, thanks to advances in mass spectrometry and chemical separation procedures that now allow all PGE to be determined at the ppb level with a precision better than 5%. The quest for the PGE composition of the Earth's primitive mantle has led to contrasting pictures. Many suites of lherzolite xenoliths from basalts erupted on continents display Pd/Ir and Pd/Pt ratios in the range shown by enstatite/ordinary chondrites ( $1.0 \pm 0.3$  and  $0.5 \pm 0.2$ , respectively; Rehkämper et al. 1997; Lorand and Alard 2001), in good agreement with the chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ratio ( $^{187}\text{Os}$  is a long-term radiogenic decay product of  $^{187}\text{Re}$ ; see Carlson et al. 2008 this volume) inferred for the primitive mantle ( $0.1296 \pm 0.0007$ ; Meisel et al. 2001). Using inductively coupled plasma-mass spectrometry (ICP-MS) and a fire-assay chemical separation procedure, Pattou et al. (1996) discovered that orogenic lherzolites from the Pyrénées (France) are characterized by Ru/Ir (2) and Pd/Ir (1.8) ratios that are moderately greater than those of carbonaceous chondrites. By analyzing xenoliths and orogenic lherzolite samples of worldwide provenance, Becker et al. (2006) obtained a PGE composition for the primitive mantle that is characterized by broadly chondritic Os, Ir, and Pt relative abundances and 20–30% higher Ru/Ir ( $2.03 \pm 0.12$ ) and Pd/Ir ( $2.06 \pm 0.31$ ) ratios. Such a primitive mantle composition does not match the composition of any known chondrite group. By contrast, it com-



**FIGURE 4** Lherzolite samples from the upper mantle. (A) Yellow-green nodules (“xenoliths”) in a basalt flow (Kerguelen Islands, Indian Ocean). COURTESY OF MICHEL GRÉGOIRE. (B) A kilometer-sized massif composed of orogenic lherzolite in the Pyrenean range (Lherz, southern France)

pares quite well with the PGE composition of Apollo XVII lunar impact melt rocks that formed in conjunction with the large, 4.0–3.8 Ga old lunar impact basins (Fig. 5). Taken at face value, the PGE composition of the impact melt rocks and the PGE signature of the hypothetical primitive mantle suggest that the meteorites that hit the Earth–Moon system had a somewhat different composition from the chondrites in our collections.

### NON-CHONDRITIC PGE RATIOS IN MANTLE-DERIVED PERIDOTITES?

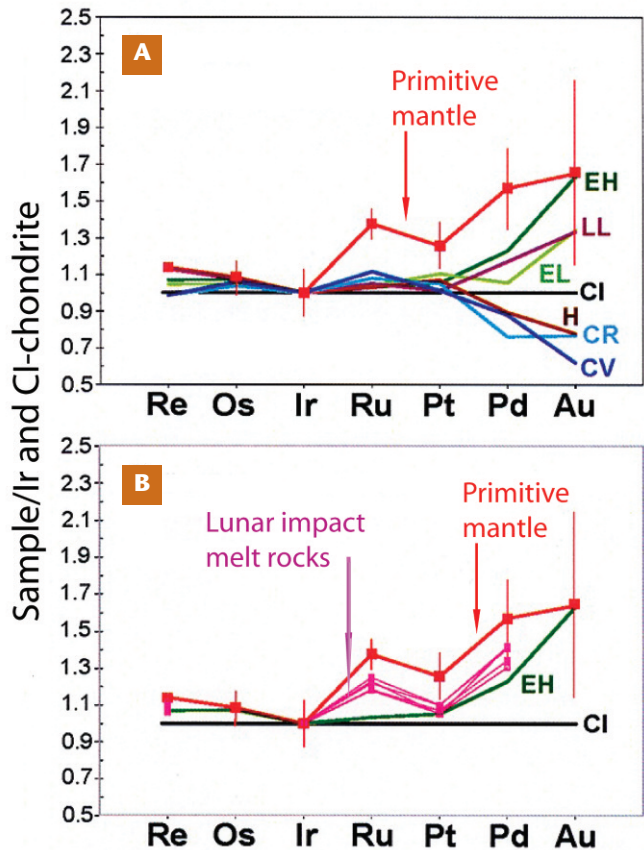
Although they display broadly chondritic PGE ratios (except for Os/Ir), very few lherzolite xenoliths transported by continental basaltic lavas have PGE concentrations similar to those of Becker et al.'s (2006) primitive mantle estimate (Fig. 6). The wide range of PGE concentrations compared to those reported in orogenic lherzolites is puzzling. Some of the lherzolitic xenoliths with low PGE contents may have lost base-metal sulfides via melt rising up through the mantle (Lorand and Alard 2001). Osmium concentrations are particularly low compared with the other PGE, which led most authors after Handler and Bennett (1999) to postulate selective loss of Os (highly volatile as an oxide) upon eruption or during alteration of the xenoliths by groundwater.

The samples used to constrain the PGE signature of the primitive mantle were stored in the rigid part of the mantle beneath the crust (the lithosphere) long after core separation and meteorite bombardment had ceased. Large volumes of the lithosphere have been affected by magmas “en route” to the Earth's surface. These magmas may have modified whole-rock Pd/Ir and Pt/Ir ratios in the mantle by precipitating Pd- and Pt-rich “basaltic” sulfides within formerly

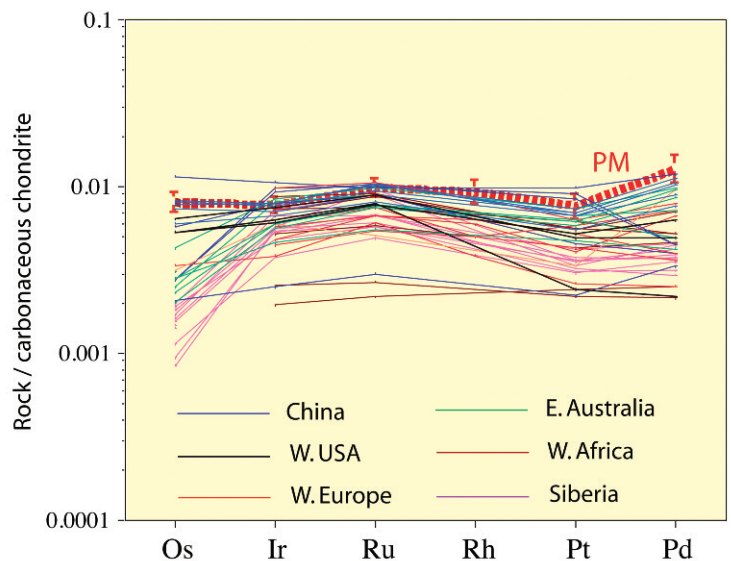
depleted residual peridotites. Physical mixing of the two sulfide populations—"restitic" and "basaltic"—identified in situ can generate whole-rock patterns akin to that postulated for the primitive mantle (FIG. 3). Rehkämper et al. (1999a) were the first to document such mixing in ocean-floor peridotites that have been extensively melted during upwelling and decompression of the mantle beneath mid-ocean ridges. In situ analyses of base-metal sulfides have provided further support for this interpretation. Alard et al. (2000) and Lorand and Alard (2001) found the Pd-rich "basaltic" sulfide population in close association with minerals diagnostic of magma circulation ("metasomatism") in the mantle beneath continents (e.g. diopside, carbonates, feldspar, apatite). Furthermore, Alard et al. (2002) measured the osmium isotope composition of sulfides in situ using a laser probe coupled with a multicollector ICP-MS. They found that the two generations of base-metal sulfides are not contemporaneous: "basaltic" intergranular sulfides are 1–2 billion years younger than "restitic" sulfides. Base-metal sulfides in peridotites from the ocean floor also preserve the two types of complementary PGE patterns, despite substantial mineralogical transformations resulting from alteration of primary minerals by seawater; moreover, "basaltic" sulfides are systematically located within sites of crystallization of magmatic or metasomatic minerals such as spinel and Ca-Al pyroxene (Luguet et al. 2003). Relatively young magmatic events that increased Pd/Ir and Pt/Ir ratios have also been documented in garnet peridotites stored beneath Archean continents (Pearson et al. 2004).

However, some issues regarding the Becker et al. (2006) primitive mantle estimate are still under debate. On the one hand, this estimate is robust because it is supported by evidence from the Moon. The suprachondritic Ru/Ir ratio cannot be explained by any process in which magmas contaminate the mantle because "basaltic" sulfides are too poor in Ir and Ru to contribute significantly to the whole-rock budget of these two PGE (FIG. 3). On the other hand, recent studies cast doubt on the primitiveness of orogenic lherzolites, the cornerstone of the Becker et al. (2006) PM estimate. Rehkämper et al. (1999a), who studied the Horoman lherzolite body (Japan), and Pearson et al. (2004), who examined the Beni-Boussera lherzolite (Morocco), concluded that PGE signatures were modified by magmas because the palladium concentrations (and Pd/Ir ratios) correlate linearly with Ca and Al, in a way not expected for mantle rocks that were processed only by partial melting. In the case of the Lherz body (southern France), the type locality of lherzolite, there is now strong evidence that lherzolites are secondary rocks resulting from the crystallization of magmas that reacted with a 2 Ga residual peridotite body (Le Roux et al. 2007). Of course, such re-enrichment processes ("refertilization") obviously call into question the link between orogenic lherzolites and primitive mantle estimates.

As for continental mantle xenoliths and peridotites from the ocean floor, comprehensive studies coupling geochemical and mineralogical approaches are required for deconvoluting the information from orogenic lherzolites. Such a study performed on a single sample from the Pyrénées identified only intergranular sulfide blebs displaying all characteristics of "basaltic sulfides," except for their PGE contents measured in situ (Lorand et al. 2008). Some blebs effectively showed the Pd-enrichment of "basaltic" sulfides while others were more akin to Pd-poor and Os-Ir-Ru-rich "restitic" sulfides. Although no mss inclusions in silicates have yet been identified, base-metal sulfides commonly enclose micrometer-sized platinum-group minerals (alloys, sulfides) very similar to the mss melting products found in highly depleted residual peridotites. The origin of these PGE micronuggets, as minerals not soluble in the low-temperature base-metal



**FIGURE 5** Ir- and chondrite-normalized PGE composition of the primitive mantle (Becker et al. 2006) compared with the main groups of chondritic meteorites (A) and with impact rocks of lunar maria (B). Note that the primitive mantle estimate does not correspond to any known chondrite composition; only the strongly brecciated rocks in the heights around lunar maria, and contemporaneous with the 3.9–3.8 Ga late heavy bombardment recorded by the Moon's surface, provide a reasonably good match with the Becker et al. (2006) primitive mantle estimate.



**FIGURE 6** Chondrite-normalized PGE abundances measured in basalt-hosted mantle-lherzolite xenoliths collected from five continents. Note that very few analyses match the Becker et al. (2006) primitive mantle estimate. Most xenoliths are significantly depleted in PGE, especially Os. DATA SOURCES: REHKÄMPER ET AL. (1997); HANDLER AND BENNETT (1999); LORAND AND ALARD (2001); PEARSON ET AL. (2004); BECKER ET AL. (2006)

sulfides in the emplaced peridotites or as high-temperature relicts from residual mantle, is a crucial issue in which we are likely to make progress over the next few years.

## CONCLUSIONS

From our knowledge of the fractionation of PGE at the microscopic scale, it seems very likely that the abundances (relative and absolute) of PGE measured in modern mantle rocks were overprinted by magmatic processes, especially melt removal and refertilization. The current primitive mantle estimate for PGE must therefore be considered a work in progress and will need reevaluation as we learn more about the behavior and location of the PGE. Nevertheless, the chondritic to slightly suprachondritic PGE ratios in fertile

lherzolites imply very efficient mixing of basaltic (crustal) material with depleted residual mantle. Our understanding of the identity of the minerals that govern the fractionation of PGE during partial melting and magmatic crystallization in the mantle is also fundamental for using PGE as geochemical tracers, not only for unravelling the early evolution of the Earth and its mantle–core system, but also for understanding the formation of PGE orebodies from mantle-derived magmas.

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