



## Invited review article

# Platinum-group element systematics and petrogenetic processing of the continental upper mantle: A review

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## ABSTRACT

The platinum-group element (PGE) systematics of continental mantle peridotites show large variability, reflecting petrogenetic processing of the upper mantle during partial melting and melt/fluid percolation inside the lithosphere. By removing Pd–Cu–Ni rich sulfides, partial melting events that have stabilized the sub-continental mantle lithosphere fractionated PPGEs (Palladium-group PGE; Pt, Pd) relative to IPGEs (Iridium-group PGE; Os, Ir, Ru, Rh). Residual base-metal sulfides (BMS) survive as enclosed IPGE-enriched Monosulfide Solid Solutions (Mss), which otherwise decompose into Ru–Os–Ir-rich refractory platinum-group minerals (PGMs) once the partial melts become S-undersaturated. The small-scale heterogeneous distribution of these microphases may cause extreme nugget effects, as seen in the huge variations in absolute PGE concentrations documented in cratonic peridotites. Magmas fluxing through the lithospheric mantle may change the initial PGE budgets inherited from the melting events, resulting in the great diversity of PGE systematics seen in peridotites from the sub-continental lithosphere. For instance, melt–rock reactions at increasing melt/rock ratios operate as open-system melting processes removing residual BMS/PGMs. Highly percolated peridotites are characterized by extreme PGE depletion, coupled with PGE patterns and Os-isotope compositions that gradually evolve toward that of the percolating melt. Reactions at decreasing melt–rock ratios (usually referred to as «mantle metasomatism») precipitate PPGE-enriched BMS that yield suprachondritic Pd/Ir and occasionally affect Pt/Ir and Rh/Ir ratios as well. Moreover, volatile-rich, small volume melts fractionate Os relative to Ir and S relative to Se, thereby producing rocks with supra-chondritic Os/Ir and S/Se coupled with supra-chondritic Pd/Ir and Pt/Ir. Major magmatic inputs at the lithosphere–asthenosphere boundary may rejuvenate the PGE systematics of the depleted mantle. Integrated studies of «refertilized» peridotites with worldwide provenance provide evidence for mixing between old PGM-rich harzburgitic protoliths and newly-precipitated BMS. Long-lived PGMs carry the Os-isotope compositions of ancient melt-depletion events into seemingly undepleted fertile lherzolites. Another diagnostic feature of major refertilization processes is the increasing modal abundance of Pt–Pd–Te–Bi or Pt–As–S microphases. Due to regional-scale refertilization processes, sizeable (> 100 km) domains of the upper lithospheric mantle are now significantly enriched in Pd, Au, Cu, Se, and other incompatible chalcophile elements that are of considerable importance in PGE-ore forming events.

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## 1. Introduction

The Earth's mantle is highly depleted in platinum group elements (PGEs) compared to the core (total PGE contents of ca 30 ng/g vs 10 mg/g; Lorand et al., 2008a; Palme and O'Neill, 2003), although not to the levels predicted by core–mantle separation models. The most robust (but still disputed) theory explains the unexpectedly high PGE concentrations in the Earth's mantle by a continuous influx of meteorites postdating core–mantle differentiation (the «late veneer» theory; Holzheid et al., 2000; Kimura et al., 1974; Lorand et al., 2008a; Palme and O'Neill, 2003; Walker, 2009).

Since the mantle is the source for most economic PGE deposits, determining the average source compositions, their spatial variations and the minerals controlling the PGE budget are essential issues for modeling the PGE contents of mantle-derived magmas that may produce such PGE deposits. Mantle peridotites (comprising lava-hosted xenoliths and tectonically emplaced orogenic lherzolite bodies) and disaggregated xenocrysts provide important insights into the sub-continental lithospheric mantle. Since pioneering papers in the 80s (Garuti et al., 1984; Lorand, 1989; Mitchell and Keays, 1981; Morgan, 1986), new and more precise analytical procedures have become available. Considerable variations in the PGE budget of mantle peridotites have been revealed over the past ten years. Mantle rocks that have reached the Earth's surface have been processed by one or several of the following petrogenetic processes, long after the Late Veneer event (Bodinier and Godard, 2003; Pearson et al., 2003): i-partial melting (as a result of adiabatic decompression of upwelling mantle or fluid input); ii-melt percolation and the so-called «refertilization» processes that may re-enrich the rigid lithosphere in basalt-forming major elements (i.e.,  $Al_2O_3$ , FeO, CaO); and iii-mantle metasomatism leading to enrichments in minor- and trace elements.

PGEs have emerged as highly sensitive geochemical tracers of these mantle petrogenetic processes (Lorand et al., 2008a and references therein). However, compared to lithophile trace elements, PGEs are non-conventional geochemical tracers of the Earth's mantle because they occur at ppb concentration levels. Moreover, they may occasionally be distributed as major elements (wt.% concentration levels) in trace platinum-group minerals (PGMs: sulfides, arsenides, tellurides, alloys, intermetallic compounds; Keays et al., 1981; Lorand et al., 2008b, 2010; Luguét et al., 2007). The aim of this paper is to summarize the spatial variations of PGE abundances in continental mantle peridotites and to present a synthesis of the processes that altered the PGE systematics inherited from the Primitive Upper Mantle (PUM). How resistant PGEs were to second-order petrogenetic processes primarily depends on what PGE-bearing minerals the mantle formed during melting, melt infiltration and subsolidus cooling. This aspect can now be addressed with a certain degree of confidence thanks to the improvements in in-situ analytical techniques for trace minerals (e.g., Laser-ablation inductively-coupled mass spectrometry (LA-ICP-MS); Field Emission Gun-Scanning Electron Microscope – FEG-SEM).

## 2. Provenance, background, source of data and analytical notes

The sub-continental lithospheric mantle (SCLM) is represented by kimberlite-hosted xenoliths of cratonic peridotites, peridotite xenoliths sampled by alkali basalts, and orogenic peridotites (Bodinier and Godard, 2003; Menzies and Hawkesworth, 1987; Pearson et al., 2003). Cratonic peridotites (mostly garnet-bearing) provide the oldest mantle fragments (up to 3.5 Ga-old) and the deepest record (up to 250 km) of the continental mantle lithosphere beneath Archean cratons (Griffin et al., 2003, 2008; Nixon, 1995; Simon et al., 2007). They record extreme degrees of depletion ranging between 30 and 50% (Pearson et al., 2003, 2004; Walter, 1998, 1999), although the exact settings that generated such high degrees of melt extraction, whether deep-seated mantle plumes that generated Archean ultramafic lavas (komatiites and komatiitic basalts) or shallow (<3 Gpa) hydrous melting above Archean subduction zones, are still debated (e.g. Arndt et al., 2009; Herzberg, 1993; Wittig et al., 2010a). Peridotite xenoliths sampled by alkali basalts provide one of the most widespread sources of information on the shallow (<100 km), post-Archean SCLM. These nodules have sampled moderately depleted lherzolites (mostly from the spinel lherzolite facies) along with subordinate amounts of refractory harzburgites, dunites, pyroxenites (Cr-diopside, Al-rich augite suites), and minor hornblendites (Pearson et al., 2003). The SCLM was also sampled by orogenic peridotite massifs tectonically emplaced by deep transcurrent faults in Phanerozoic mountain belts (Bodinier and Godard, 2003). Orogenic peridotite massifs and basalt-hosted peridotite are probe on off-cratonic continental mantle lithosphere. Orogenic peridotites may also show exposures of subducted oceanic crust + lithosphere sections (like in western Norway; Menzies and Dupuy, 1991; Spengler et al., 2006 and references therein), which are not discussed in the present paper that focuses on the continental lithospheric mantle.

Extensively used for dating geological events, the Re–Os chronometer has considerably increased the number of Os and Re data (more than 1000 analyses now available). The other five PGEs have been determined in more than six hundreds samples. Becker et al. (2006) and Fischer-Gödde et al. (2011) discussed the reliability of the different analytical methods used to analyze ultra-trace levels of PGE in silicate rocks of the mantle (see also Lorand et al., 2008b; Meisel et al., 2003). They suggested that acid digestion (hot aqua regia) of the sample in Carius Tube (CT) or in a high-pressure asher (HPA, the high-pressure dissolution design) coupled with isotope dilution (ID), solvent extraction, chromatographic separation and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) provide the most reliable results as they generate very low blank levels (a few tens of ppt) and are not affected by any element loss during the chemical separation step. Rhodium, which is mono-isotopic, was only recently included in ID-CT/HPA-ICPMS procedures (Fischer-Gödde et al., 2011; Meisel and Moser, 2004). Another popular separation procedure involves fire assay of the sample and collection of PGEs in a nickel sulfide button, followed by a Te-coprecipitation step of the PGEs and ICP-MS measurements by reference to external calibration standards (the NiS fire assay-Te

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