Platinum-group element micronuggets and refertilization process in Lherz orogenic peridotite (northeastern Pyrenees, France)

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Abstract

Highly siderophile elements (Platinum-group elements, Au and Re) are currently assumed to reside inside base metal sulfides (BMS) in the convecting upper mantle. However, fertile lherzolites sampled by Pyrenean orogenic peridotite massifs are unexpectedly rich in 0.5–3 μm large micronuggets of platinum-group minerals (PDM). Among those, sulfides from the laurite-erlichmanite series (Ru, Os(Ir)S(As)2), Pt–Ir–Os alloys and Pt–Pd–Te–Bi phases (moncheite–merenskyite) are predominant. Not only the BMS phases but also the PDM micronuggets must be taken into account in calculation of the PGE budget of orogenic fertile lherzolites. Laurite is a good candidate for equilibrating the whole-rock budget of Os, Ir and Ru while accounting for supra-chondritic Ru/Ir ratios. Textural relationships between PGMs and BMS highlight heterogeneous mixing between refractory PGMs (laurite/Pt–Ir–Os alloys) inherited from ancient refractory lithospheric mantle and late-magmatic metasomatic sulfides precipitated from tholeitic melts. “Low-temperature” PGMs, especially Pt–Pd bismuthotellurides should be added to the list of mineral indicators of lithospheric refertilization process. Now disseminated within fertile lherzolites, “lithospheric” PGMs likely account for local preservation of ancient Os model ages (up to 2 Ga) detected in BMS by in-situ isotopic analyses. These PGMs also question the reliability of orogenic lherzolites for estimating the PGE signature of the Primitive Silicate Earth.

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1. Introduction

As highly siderophile elements, platinum-group elements (PGEs), Au and Re, are presumably concentrated in the metallic core of the Earth. It is commonly inferred that the late meteoritic influx that hit the earth–moon system after accretion and core formation delivered supplementary PGE to the hypothetical Primitive Upper Mantle (PUM) of the Earth (Morgan, 1986; Lorand et al., 2008a and reference therein). Updated estimates of the PGE composition of the PUM identified reproducible (20–30%) deviations from the canonical chondritic model in the light/heavy PGE ratios (i.e. Ru/Ir, Rh/Ir, Pd/Pt; Becker et al., 2006). However, PGE’s are ultra-trace elements in chondritic model in the light/heavy PGE ratios (i.e. Ru/Ir; Rh/Ir; Pd/Ir).

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phases) per standard-size polished thin section of FON-B 93, a fertile lherzolite from Fontêtre Rouge, near Lherz. This PGM assemblage accounts for c.a. 90% of the whole-rock Pt budget, in agreement with previous estimates performed on orogenic lherzolites (e.g. Luguet et al., 2004).

The actual abundance of micrometric PGM in fertile orogenic lherzolites, their contribution to the whole-rock PGE budget and their petrogenetic significance is poorly understood. To address the issue in a more quantitative way, we have performed an integrated, multi-technique study on 17 mantle peridotites collected mainly from the Lherz orogenic massif (North Eastern Pyrenees, France), the type-locality of lherzolite and one of the best studied in terms of petrogenetic evolution. The PGMs were searched for using a combination of reflected light microscopy, high-resolution scanning electron microscope (FEG-SEM) and LA-ICPMS analyses (14 samples). LA-ICP-MS is a powerful tool for detecting such minerals which create PGE concentration spikes in time-resolved spectra (Ballhaus and Sylvester, 2000). We provide evidence that 1) PGM and BMS are not necessarily co-genetic; 2) Ru–Os–Ir PGMs, identified here for the first time in fertile lherzolites, were inherited from refractory mantle peridotites; and 3) PGM fractionate some whole-rock PGE ratios that are considered to be signature of the Primitive Silicate Earth.

2. Geological setting

The Lherz orogenic peridotite massif and its cluster of peridotite outcrops (Freychnêde, Fontêtre Rouge) are three of the 40 or more bodies of mantle rocks spatially associated with high-grade metamorphic rocks of the granulite facies in the North Pyrenean Zone. It was emplaced from the mantle c.a. 100 Ma ago by the movement of the Iberian plate relative to Europe, which resulted in crustal thinning associated with successive opening and closing of elongated, asymmetrical pull-apart mезozoic sedimentary basins (Fabriès et al., 1991; Lagabrielle and Bodinier, 2008 and ref. therein).

Pyrenean orogenic peridotites consist mainly of weakly (<25%) serpentinitized spinel lherzolites (10–16 wt.% cpx). Clinopyroxene-poor lherzolites (5–10 wt.% cpx) are much rarer and true harzburgites (cpx <5 wt.%cpx) are known only in the Fontêtre Rouge and Lherz massifs (Fabriès et al., 1991). The Lherz massif displays the best exposure of boudinaged lenses of highly refractory harzburgites, intermingled on a decametric scale with fertile lherzolites. The most fertile lherzolites (15% clinopyroxene) have long been interpreted as pristine mantle, only weakly affected by partial melting whereas harzburgites record a decametric scale with fertile lherzolites (cpx-rich harzburgites, 82–4; 71–322; 12–1; 71–107; fertile lherzolites 71–321, 71–326, 86–V2–5 and 71–324) and the two Freychinêde lherzolites are “historic” samples, already analysed for whole-rock sulfur contents and BMS mineralogy (Lorand, 1989a,b), Re-Os isotopic compositions (Reisberg and Lorand, 1995) and PGE systematics (Pattou et al., 1996; Lorand et al., 1999; Becker et al., 2006).

Site 2 and Site 4 samples were analysed for S using iodometric titration of the SO₂ produced by combustion of 500 mg powder aliquot at the National Museum of Natural History (see Gros et al., 2005 for further details). PGEs were separated at the MNHN from powder aliquots of 15 g each by a NiS–fire assay — Te coprecipitation procedure as described by Gros et al. (2002) and modified by Lorand et al. (2008b) to improve the recovery of PGE (i.e. second NiS–fire assay step and amount of Te increased to 28 ml). The analyses were performed using a FIONS VG 353 PlasmaQuad PQplus inductively coupled plasma mass spectrometer (ICP-MS) (University of Montpellier II and National Museum of Natural History, Paris). Sample 82–4, already analysed by Lorand et al. (1999) and Becker et al. (2006) was reanalysed by isotope dilution-ICP-MS (Thermo-Finnigan Element 2 magnetic-sector ICP-MS) at the Northern Centre for Isotopic and Elemental Tracing (NCIET) at the University of Durham (UK). Sample digestion was performed overnight at 300 °C and 100 bars in Anton Paar HPA-S pressure-sealed quartz vessels containing 7.5 ml reverse aqua-regia. Details on the separation procedure and analytical conditions were given in Lorand et al. (2008b) and in Luguet et al. (2009).

Platinum group minerals (PGM) were located on carefully polished 200 μm-thick standard-sized (40 × 25 mm) sections using reflected light microscopy and high-resolution scanning electron microscope (Supra™ 55VP Zeiss FEG-SEM; Pierre and Marie Curie University, Paris VI) equipped with an energy dispersive Si(L) detector with a resolution of 129 eV full width at half maximum at the Fe peak. The SEM examinations were carried out at an acceleration voltage of 15 kV and a working distance of 8 mm to identify platinum-group minerals qualitatively in the backscattered mode. Manual scan of the thick sections in the backscattered mode were preferred over automated particle search procedures that may

3. Petrographical and analytical notes

The seventeen samples selected for the present paper comprise two lherzolites from Freychinêde and fifteen lherzolites and harzburgites from Lherz. The degree of serpentinisation ranges from 15 to 30% for the harzburgites to 5–20% for the lherzolites (Lorand, 1989a). At Lherz, two harzburgites (04lh13; 04lh11), one cpx-poor lherzolite (04lh08; or cpx-rich harzburgites) and two fertile lherzolites (04lh815; 04lh15) are reference samples from the Le Roux et al. (2007) study of Site-2 section across one harzburgite-lherzolite contact (hereafter referred to as Site-2 samples). Samples 04lh37 and 04lh39 are lherzolites from Site-4 of the same study (hereafter referred to as Site-4 samples). The other Lherz samples (cpx-rich harzburgites, 82–4; 71–322; 12–1; 71–107; fertile lherzolites 71–321, 71–326, 86–V2–5 and 71–324) and the two Freychinêde lherzolites are “historic” samples, already analysed for whole-rock sulfur contents and BMS mineralogy (Lorand, 1989a,b), Re-Os isotopic compositions (Reisberg and Lorand, 1995) and PGE systematics (Pattou et al., 1996; Lorand et al., 1999; Becker et al., 2006).
not detect particles on the nanometer scale in accessory BMS, despite strong contrast in atomic numbers between host and included PGM.

Platinum-group element contents of base metal sulfides were determined along with a few other trace elements (Te, Bi, Pb) by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in fourteen samples from Lherz that displayed BMS grains large enough (>100 µm) to be probed. A GEOLAS excimer UV laser operating at 193 nm, coupled with a Thermo-Finnigan Element 2 magnetic-sector ICP-MS inductively coupled plasma mass spectrometer (ICP-MS) (University of Montpellier II) was used. Analytical conditions were reported in Lorand et al. (2008b). The laser beam diameter was set up at 51 µm, 5 Hz laser frequency and a beam energy of about 15 J/cm². Accuracy was tested with in-house standards (NiS beads doped with SARM 7 rock standard powder; SABS website 2005) analysed separately at Montpellier and at the “Museum Royal de l’Afrique Centrale” at Tervuren (Belgium); both sets of analyses produced very similar results (generally differing by no more than 10%). Measured concentrations of Au and PGE fit the theoretical concentrations at 1 sigma level (Table 1). Concentrations of Os, Ir, Ru and Rh show the lowest reproducibility and thus, the largest relative standard deviation (up to 70% for Ru and Ir). This results from mineralogical inhomogeneities in NiS beads (Gros et al., 2002) possibly linked to non-homogeneous mixing of powder particles inside the NiS too.

4. Results

4.1. Whole-rock PGE and S abundances and BMS mineralogy

Lherzolites, cpx-rich harzburgites and harzburgites are characterized by different whole-rock PGE systematics. The most fertile lherzolites show CI-chondrite normalized PGE abundance patterns similar to those inferred for the Primitive Upper Mantle (Becker et al., 2006), i.e. positive anomalies of Ru, Rh and Pd relative to heavy PGEs (i.e. Ru/IrN and Pd/IrN > 2; Ru/IrN = 0.30–0.38; N = CI-chondrites-normalized; Fig. 1A). The two Site-2 harzburgites (04Lh13 and 04Lh11) display negatively trending Pd-depleted CI-chondrite normalized patterns (Pd/IrN = 0.33–0.21; Pd/PtN = 0.32–0.50), coupled with very low S contents (38–51 ppm; Table 2), as is expected for solid mantle residues after 20–25% of partial melting (Lorand et al., 1999). Similar patterns were reported for BMS-free harzburgites collected in the thickest harzburgite lenses from the south-eastern part of the Lherz massif (Luguet et al., 2007). The three cpx-rich harzburgites share features with both the harzburgites (i.e. a strong Pt-depletion relative to Ir; Pt/IrN = 0.54–0.68) and the lherzolites (Pd enrichment relative to Pt; Pd/PtN = 0.96–1.18; Fig. 1B), while displaying intermediate S contents (56–80 ppm).

Regardless of the whole-rock S contents, BMS are 20–300 µm across polyhedral (not spherical) blebs with convex-inward grain boundaries (Fig. 2). BMS blebs occur almost exclusively in intergranular pores, within the same microstructural sites as major minerals involved in the refertilization process, i.e. opx, vermicular Al-spinel (which represents no more than 3% of host rock modal compositions) and cpx. A higher proportion of BMS was found to be adjacent to olivine in the harzburgites and the cpx-rich harzburgites, a likely consequence of the higher olivine modal abundances. The major

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<th>Table 1</th>
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<tr>
<th></th>
<th>Os (ppm)</th>
<th>Ir (ppm)</th>
<th>Ru (ppm)</th>
<th>Rh (ppm)</th>
<th>Pt (ppm)</th>
<th>Pd (ppm)</th>
<th>Au (ppm)</th>
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<tbody>
<tr>
<td>SARM-7-10 Montpellier</td>
<td>0.17</td>
<td>0.38</td>
<td>1.30</td>
<td>0.75</td>
<td>7.49</td>
<td>3.95</td>
<td>0.66</td>
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<td></td>
<td>±0.10</td>
<td>±0.26</td>
<td>±0.90</td>
<td>±0.30</td>
<td>±0.98</td>
<td>±1.55</td>
<td>±0.19</td>
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<td></td>
<td>±0.13</td>
<td>±0.25</td>
<td>±1.06</td>
<td>±0.42</td>
<td>±1.54</td>
<td>±1.33</td>
<td>±0.22</td>
</tr>
<tr>
<td>Theoretical concentrations</td>
<td>0.12</td>
<td>0.28</td>
<td>0.98</td>
<td>0.56</td>
<td>7.24</td>
<td>2.96</td>
<td>0.6</td>
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<tr>
<td>SARM-7-1 Montpellier</td>
<td>0.33</td>
<td>0.32</td>
<td>1.10</td>
<td>0.60</td>
<td>8.76</td>
<td>3.89</td>
<td>0.69</td>
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<td></td>
<td>±0.11</td>
<td>±0.11</td>
<td>±0.48</td>
<td>±0.22</td>
<td>±2.86</td>
<td>±0.39</td>
<td>±0.23</td>
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<tr>
<td></td>
<td>±0.14</td>
<td>±0.11</td>
<td>±0.48</td>
<td>±0.22</td>
<td>±2.86</td>
<td>±0.39</td>
<td>±0.23</td>
</tr>
<tr>
<td>Theoretical concentrations</td>
<td>0.34</td>
<td>1.176</td>
<td>0.61</td>
<td>8.64</td>
<td>3.55</td>
<td>0.552</td>
<td>SABS (2005)</td>
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</table>
BMS are pentlandite-Pn (Fe/Ni= 1.15 ± 0.3) and chalcopyrite-Cp (Cu/Fe = 0.96 ± 0.04), representing 80–95% and 5–15% by volume, respectively. Bornite, pyrrhotite, pyrite and mackinawite are minor sulfides (Lorand, 1989b). Both Pn and Cp display nice wetting features (dihedral angles < 60°) against olivine neoblasts. Some samples show BMS grains of two different sizes, i.e. large grains (generally located in sp–opx–cpx clusters) surrounded by clouds of tens of minute (<30 µm) sulfide blebs, which result from mechanical dispersion of sulfide melts by the strong plastic deformation and recrystallization of silicates.

4.2. Platinum-group minerals

Platinum-group minerals (PGM) were identified in all of the 17 samples studied. Ninety five PGM grains ranging in size from

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<th>Sample</th>
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<th>Abundance</th>
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**Table 2**

Whole-rock PGE analyses. H = harzburgite; C+H = clinopyroxene-rich harzburgite; L = lherzolite; C+L = clinopyroxene-rich lherzolites.

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<th>Sample</th>
<th>Type</th>
<th>Abundance</th>
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1 This study; 2 Becker et al. (2006); 3 Lorand et al. (1999). n.a.: not analysed.

**Fig. 2.** Photomicrographs of base metal sulfides-BMS (A BSE image; B to D: plane polarized reflected light images). A: polyhedral pentlandite grain displaying very low dihedral angles with matrix silicates; B: two-phase intergranular BMS (pentlandite-Pn + chalcopyrite-Cp); C: Polyhedral pentlandite–chalcopyrite intergrowth illustrating the high wetting capacity of Cu–Ni-rich sulfide melts in the mantle; D: disaggregated BMS grains in a highly deformed lherzolite; note the very small satellite BMS blebs all around the largest grains.
0.25×0.1 µm to 16 µm×1.4 µm were detected by SEM operating in the BSE mode inside or in the immediate vicinity of BMS blebs. Quantitative analysis by electron microprobe was precluded by the very small grain size of PGMs and their location inside or at the vicinity of BMS which generated continuous fluorescence on PGM analyses. According to EDS spectra (not shown), PGMs mainly consist in sulfides from the laurite-erlichmanite series \([\text{Ru,Os(Ir)}]_2\text{S(As)}_2\), Pt–Ir–Os rich alloys and Pt–Pd–Te–Bi phases (moncheite–merenskylite). The other PGMs identified in Pyrenean peridotites are Pt arsenides/sulfarsenides (sperrylite), Cu–Pt–Ir sulfides (malanite), Pd–Ni–S (braggite), Pd–Cu compounds, Pt–Fe alloys and native gold. Additional PGM micronuggets (56) were detected by in-situ LA-ICPMS analyses. When drilling through a micronugget, this latter generates concentration spikes in time-resolved spectra which allow qualitative assessment of which PGE is hosted in the micronuggets. In-situ analyses confirm the results of EDS spectra, namely the predominance of Pt–Ir–Os alloys and Pt–Pd–Te–Bi phases over the other PGM species. Pt–Ir–Os alloys display variable Ir/Os ratios. Native gold is not uncommon while native platinum is exceptionally scarce.

Pyrenean peridotites display a continuum of PGM assemblages which vary sympathetically with whole-rock S contents, and thus BMS modal abundances (Fig. 3). The BMS-poor residual harzburgites (04Lh11 and 04Lh13) show very similar PGM assemblages as the BMS-free harzburgites analysed by Luguet et al. (2007). Laurite coexists with Pt–Ir–Os alloys and Cu–Pt-rich sulfides of the malanite–cuprorhodsite series; it can generate huge concentration spike in the time-resolved spectra for Os–Ir–Ru–As (Fig. 4A). Cpx-rich harzburgites, of intermediate BMS content, differ from the harzburgites by occurrence of a few Pt- and Pd-rich PGMs (bismuthotellurides, sulfides and alloys; e.g. 71–322), coexisting with laurite and Pt–Ir–Os alloys. The relative abundance of laurite drops in the lherzolites whereas that of bismuthotellurides significantly increases along with the abundance of BMS. The PGM assemblages in the Lherz lherzolites are dominated by Pt–Ir–Os alloys and Pt–Te–Bi phases, in agreement with previous observations on FON B-93 (Lorand et al., 2008b). The only PGM detected in some samples, especially poor in PGM but very rich in BMS (04Lh37) were Pt–Te–Bi phases. Platinum arsenides/sulfarsenides and discrete native gold were detected in PGM-rich samples.

Fig. 3. Evolution of PGM assemblages as a function of whole-rock S contents. Note that laurite modal proportions decrease as whole-rock S concentrations (and thus BMS modal abundance) increase. The minerals showing Pt–Pd–Te–Bi combinations predominate in the PGM assemblages of lherzolites. The alloys of Pt–Ir–Os do not show clear trend, being present in similar proportions from the lherzolites to the most depleted harzburgites. N = number of PGM grain per sample.

Fig. 4. Time-resolved LAM-ICP-MS spectra collected during three analyses of pentlandite. The huge spikes of Ru, Ir and Os concentrations, coupled with a minor As concentration spike identify a laurite nugget that contains trace amounts of Pt and Pd in A. B displays two spikes of Pt, Ir and Os concentrations corresponding to Pt–Ir–(Os) micronuggets; the second one is associated with a Pt–Te–Bi phase. C corresponds to analysis of a pentlandite-chalcopyrite bleb containing a mix of Pt–Ir–(Os) alloy and Pt–Te–Bi phase.
Although PGM are systematically associated with BMS grains, the total number of PGM detected in a single sample does not correlate with whole-rock S contents. Sample 71-322, a Lherz cpx-harzburgite is as rich in PGM as the lherzolites in spite of markedly lower S contents (Fig. 3). Conversely, S-rich lherzolites may be very PGM-poor (04Lh39; 321 ppm S; 1 PGM). In addition to real random distribution and strong random sectioning effect on micrometer-sized mineral, the between-sample variation in PGM modal abundance seems to correlate with the intensity of plastic deformation. The PGM-rich samples (71-322, 04LH15, LH 815 and 71-339) are sub-mylonitic samples more extensively deformed and recrystallized, and richer in minute (<50 µm) sulfide blebs than the other samples. The high abundance of PGM in those samples is confirmed by a larger number of concentration spikes in time-resolved laser ablation spectra. Each of the 8 BMS grains analysed in-situ in LH15 generated PGE concentration spikes. Some grains display evidence of at least three PGMs located inside the analysed BMS grain (Fig. 4B).

Although very scarce in fertile lherzolites, laurite was detected in BSE images of 71-339 and in three LAM-ICPMS signal vs. time diagrams of Lherz lherzolites (04 LH08; 04Lh815; 86-V2-5. In 71-339, laurite and Pt–Ir–Os alloys preferentially occur within small-sized (<80 µm) satellite sulfide grains around larger BMS blebs. Laurite crystals (3 × 2 µm in maximum dimensions) occur as a combination of cubic and octahedral morphology, often Os-enriched (Os/S) towards grain rims. It has been observed as (i) cubes included in Pn cores (Fig. 5A), (ii) as external granules sharing one face with matrix silicates or Al–Cr-spinel (Fig. 5A, C) or (iii) as discrete, euhedral grains sharing just one face with BMS, which may be Pt or Cp (Fig. 5D). The sequence from Fig. 5D to A likely corresponds to different stage of entrapment of laurite by BMS blebs. It is worth noting that very few laurite were detected in LAM-ICPMS time-resolved spectra. This is in agreement with the preferred location of laurite nearby very small BMS grains which are too small to be analysed with laser ablation techniques.

Unlike laurite, in-situ analyses detected numerous concentrations spikes corresponding to Pt–Ir–Os alloys and Pt–Te–Bi phases. Pt–Ir–Os alloys tend to be acicular (up to 10 × 0.1 µm). These single-phase grains are concentrated preferentially with small-sized pentlandite blebs (average diameter of 17 grains: 29 ± 22 µm). Pt–Ir–Os alloys are commonly associated with laurite inside the same BMS (Fig. 5A), as inclusions in homogenous Pn cores (Fig. 5E) or as external needles adhering to Pn (Fig. 5F). Pt–Ir–Os alloy inclusions in Cp–Pn intergrowth are very scarce. Overall, PGE spikes are randomly distributed in time-resolved spectra. In the mylonitized samples, spikes of Pt–Ir–Os alloys occur preferentially as the S signal is decreasing rapidly. This observation is consistent with the BSE images. Both suggest that Pt–Ir–Os alloys are adhering to, but are not fully enclosed by BMS.

Pd–Te–Bi phases are intimately associated with Cp or Cp–Pn intergrowths. Pt-rich tellurides were commonly found to occur in pentlandite-chalcopyrite intergrowths as thin (<1 µm thick), cleaved trigonal sub-equant platelets (Fig. 5H). Aside their marked preference between Cp and Pn. In sample 71-339, a complex, four-phase PGM assemblage displays a Pt–Fe alloy and a Pt–bismuthotelluride rod protruding from an euhedral crystal of laurite + Pt–arsenide (Fig. 5G).

Such four-phase PGM composite inclusions share one face with Al–Cr-spinel.

5. Discussion

5.1. Significance of PGM composition and mineralogy in the petrogenetic history of the Pyrenees Orogenic Peridotite Massifs

The Lherz and Freychinède peridotites show the widest range of «primary» PGM combinations yet reported in fertile mantle peridotites, with some minerals (sulfides of the laurite-erlichmanite series) reported for the first time in such rocks. Our results shed some new light on the origin of PGMs as a whole in orogenic lherzolites. However before discussing their origin, it is necessary to recall some basic features of mantle-derived BMS. Phases like monoclinal pyrrhotite, pentlandite and chalcopyrite are low-temperature minerals, not stable under P–T conditions of the upper mantle. Paragenetic succession of BMS has been extensively discussed for pentlandite-rich (80–95% Pn; 5–15% Cp; Table 3) assemblage such as those studied here (Lorand et al., 2008b). These assemblage ultimately derived from metal-rich (i.e. metal/sulfur atomic ratio >1) Cu–Ni sulfide melt (Alard et al., 2000, 2005; Ballhaus et al., 2001; Luguet et al., 2003; Lorand et al., 2008a,b). At 1.5 Gpa, the average pressure of equilibration of Pyrenean peridotites within the lherzothorphic continental mantle (Fabries et al., 1991), this assemblage should be molten at ca. 1150 ± 50 °C (Bockrath et al., 2004a,b). On cooling down from 1150 to 1000 °C, this composition is expected to precipitate almost equal proportions of a Ni-rich monosulfide solid solution (22–25 wt.% Ni) with metal/sulfur (M/S) ratio of 0.3, and a Ni-rich sulfide melt more metal-rich than the Mss, which will subsequently crystallizing the high temperature form of haxeledioidite (Hx) at 860 °C. On further cooling, the sulfide melt is also enriched in Cu until Iss (Intermediate solid solution) crystallizes at 880–840 °C (Peregoedova and Ohnenstetter, 2002). A reaction between Hz-Iss and Mss at T ~ 600 °C produced massive pentlandite, while chalcopyrite is stable below 557 °C (Fleet, 2006 and ref. therein). Note that a slightly different cooling path was deduced by Lorand (1989b) for some pyrite-rich Pyrenean lherzolites that exsolved pentlandite at lower temperature (<300 °C). As pyrite is either absent or present in very minor proportion, the 600 °C figure is considered to be more likely for the Lherz and Freychinède samples studied here. In both paths, some readjustment of Ni and Cu distribution between Cp and Pn occurred until closure temperature below 100 °C is reached (Lorand, 1989b).

The solubility of Os, Ir and Ru and Rh in (Fe–Ni)–S monosulfide (solid or molten) is several thousands of ppm to several percents (e.g. Alard et al., 2000; Brenan and Andrews, 2001; Brenan, 2002; Bockrath et al., 2004; Mungall et al., 2005; Ballhaus et al., 2006). Pentlandite, the major low-temperature BMS (>80 vol.%) in Lherz lherzolites can dissolve ten percent levels of Ru, Rh and Pd, as shown by experimental works (Makovicky et al., 1986) and natural occurrence of ruthenium and/or rhodium equivalent of low-temperature pentlandite have been reported in PGE ores (Cabri, 1992; Augé, 1988; Zacarini et al., 2005). Even at 25 °C the Ru, Ir and Os content of Pentlandites from PGE ores is 2–4× the Ru–Ir–Os concentration range measured within Lherz pentlandites (4–55 ppm; Table 3) (Cabri, 1992; Ballhaus and...
Table 3

Contribution of BMS to the whole-rock PGE budget of Pyrenean orogenic peridotites (concentration in ppm).

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<tr>
<th></th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
<th>N</th>
</tr>
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<tr>
<td>82-4 (0.024 wt.% suldes)</td>
<td>18.7</td>
<td>15</td>
<td>32</td>
<td>3.8</td>
<td>19</td>
<td>12.2</td>
<td>5</td>
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<tr>
<td>Calculated BMS</td>
<td>±6.0</td>
<td>±4.3</td>
<td>±8.0</td>
<td>±1.35</td>
<td>±4.0</td>
<td>±3</td>
<td></td>
</tr>
<tr>
<td>Measured BMS</td>
<td>8.63</td>
<td>5.44</td>
<td>10.5</td>
<td>2.11</td>
<td>2.75</td>
<td>32.3</td>
<td></td>
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<tr>
<td>±1.8</td>
<td>±5</td>
<td>±2</td>
<td>±1.5</td>
<td>±6</td>
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71-322 (0.016-0.011 wt.% suldes)

<table>
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<th></th>
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<th>Ir</th>
<th>Ru</th>
<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
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<tr>
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<td>26.7</td>
<td>30.3</td>
<td>53.3</td>
<td>100.7</td>
<td>45.3</td>
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<tr>
<td>±18</td>
<td>±20</td>
<td>±25</td>
<td>±5</td>
<td>±12</td>
<td>±11.7</td>
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<tr>
<td>Measured BMS</td>
<td>2.00</td>
<td>2.57</td>
<td>5.36</td>
<td>1.62</td>
<td>1.26</td>
<td>28.40</td>
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<tr>
<td>±0.9</td>
<td>±1.65</td>
<td>4.38</td>
<td>±1</td>
<td>±1.29</td>
<td>±8.56</td>
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404Lh08 (0.044 wt.% suldes)

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<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
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<tbody>
<tr>
<td>Calculated BMS</td>
<td>7.30</td>
<td>4.06</td>
<td>5.88</td>
<td>1.90</td>
<td>0.87</td>
<td>12.82</td>
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<tr>
<td>±2.1</td>
<td>±2.20</td>
<td>±3.18</td>
<td>±0.85</td>
<td>±0.57</td>
<td>±2.20</td>
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404Lh15 (0.06 wt.% suldes)

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<th>Pt</th>
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<tbody>
<tr>
<td>Calculated BMS</td>
<td>7.74</td>
<td>6.58</td>
<td>6.34</td>
<td>2.0</td>
<td>0.36</td>
<td>12.99</td>
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<tr>
<td>±2.62</td>
<td>±3.27</td>
<td>±4.37</td>
<td>±0.54</td>
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404Lh15/0.06 wt.% suldes

<table>
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<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
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<tr>
<td>Calculated BMS</td>
<td>6.5</td>
<td>5.9</td>
<td>11.32</td>
<td>2.25</td>
<td>11.09</td>
<td>10.5</td>
<td>6</td>
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<tr>
<td>±3.39</td>
<td>±0.90</td>
<td>±2.23</td>
<td>±1.50</td>
<td>±0.42</td>
<td>±0.33</td>
<td>±5.15</td>
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404Lh15/0.06 wt.% suldes

<table>
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<tr>
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<th>Ir</th>
<th>Ru</th>
<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
<th>N</th>
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<tbody>
<tr>
<td>Calculated BMS</td>
<td>5.28</td>
<td>4.10</td>
<td>6.17</td>
<td>1.90</td>
<td>0.24</td>
<td>22.04</td>
<td></td>
</tr>
<tr>
<td>±2.84</td>
<td>±2.70</td>
<td>±3.70</td>
<td>±3.07</td>
<td>±0.99</td>
<td>±0.08</td>
<td></td>
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</table>

Sylvester, 2000; Godel et al., 2007; Godel and Barnes, 2008 and ref. therein).

Of course, owing to their low PGE content, BMS residing in the upper mantle are expected to be undersaturated with respect to PGM (Table 3). The sulfide-PGM assemblages of mantle samples actually reflect a complex series of events. Basically, three episodes can be identified at which the sulfides and the PGE phases could have formed (1) during the partial melting and melt depletion events which eliminated the BMS from the lithospheric protolith of (2) the refertilization process that added elements like Se, As, Sb, Te, and Bi (chalcogenes and semimetals) which were able to scavenging PGE from BMS and (3) crystallization of the base metal sulfides during decompression and emplacement of the peridotite bodies within the crust, as temperature decrease tends to expel PGE formerly in solution in BMS.

5.2. BMS, Pt–Pd–Te–Bi phases and the refertilization model

Of likely subsolidus origin are Pt–Pd–Te–Bi phases (and Pt arsenides too) that are systematically enclosed in BMS. Those PGMs and the BMS phase are co-genetic, as suggested by the coupled increase in the modal abundances of both minerals (Fig. 3): semi-metallic anions of Te, Bi, and As were delivered (like S), by the tholeiitic melt involved in the refertilization process that affected the harzburgitic protolith.

Textural (i.e. location in the interstitial pores of the rocks, within the same microstructural sites as major minerals involved in the refertilization process) and compositional features lead us to interpreted BMS in Lherz and Freychinetè Iherzolites as crystallization products from an exotic component, for instance the tholeiitic melt that refertilized the harzburgitic protolith in the Le Roux et al. (2007, 2008, 2009) model. Our interpretation of late-magmatic/metasomatic origin is supported by 1) the shape of BMS blebs and their mineral assemblages (pentlandite–chalcopyrite intergrowths, occasional bornite) are typical of Cu–Ni sulfide melt already identified in abyssal and continental mantle peridotites that reacted with basaltic melts and 2) Lherz pentlandites display only Pd-enriched (i.e. Type-II; Fig. 6) chondrite-normalized PGE patterns characterizing metasomatic sulfides in oceanic peridotites refertilized by basaltic melts (Luguet et al., 2003, 2004; Alard et al., 2005). Of specific interest in this discussion is the origin of BMS in the cpx-rich harzburgites and the harzburgites. Melting models suggest that those refractory rocks should be characterized by Cu-poor Mss inclusions (or reequilibration products of this mineral, i.e. Pn–Po intergrowths) displaying a gradual depletion in Pt and Pd (Pd/IrN >0.2; Pt/IrN <0.5) (Ballhaus et al., 2006). Such enclosed Mss are commonly preserved by peridotite xenoliths in alkaline lavas (e.g. Alard et al., 2000; Lorand and Alard, 2001). However, at Lherz, BMS in harzburgites are in no way different from BMS in Iherzolites. They are composed of intergranular Pentlandite-Pn blebs displaying nice wetting features of metal-rich sulfide melts and constant Cu/S ratios (0.1–0.2) with no evidence of trapped Mss. The refertilization model that implies a unique source for the BMS (i.e. the tholeiitic melt) accounts for such constant mineralogical features from the Iherzolites to the S-depleted harzburgites. The REE variation in harzburgitic Cpx indicates that small melt fractions residual after the refertilization reaction migrated in the harzburgite protolith (Le Roux et al., 2007, 2009), thus precipitating Pd-rich sulfides in formerly Pd-depleted peridotites. These late-magmatic BMS may account for whole-rock Pd/Pn ≥1 much better than partial melting models (cf. Luguet et al., 2003) because Pd is more incompatible than Pt.

Platinum does not enter the octahedral site of pentlandite (nor chalcopyrite), the two main sulfides in the samples under discussion. All Pyrenean pentlandites analysed in-situ are strongly depleted in Pt (by factors of up to 100) relative to the other PGEs (Fig. 6). This Pt deficit is also noted in sulfides from PGE deposits (see Ballhaus and Ryan, 1995). It reflects exsolution of Pt–Fe alloys when melt recrystallizes to Po and Pn and when Lss recrystallizes to Cp. Platinum was also scavenged from BMS to form PtAs, PtSS and Pt tellurides which are rather stable once formed. At Lherz, like in sample FON J-93 from Fontètte Rouge (Lorand et al. 2008b), the preferential occurrence of bismuthotellurides in isolated Cp or Cp–Pn intergrowths is consistent with the strong affinity of these highly incompatible elements for Cu-rich sulfide melts (Yi et al., 2000). Semi-metals form soft ligands that stabilize Pt and Pd in the sulfide melt, thus further decreasing their Pn/sul/sulfide melt partition coefficients (Ballhaus and Sylvester, 2000). Sulfide melt and telluride melt are fully miscible.
above 1150 °C (Helmy et al., 2007). For c.a. 70,000 ppm of Te + Pt + Pd, the telluride melt is saturated with respect to Pt-telluride at T > 1015 °C while Pd–Ni–telluride saturation is shifted down to subsolidus temperatures (<700 °C; Gervilla and Kojojen, 2002). However, saturation in Pt–Te–(Bi) phases in Pyrenean peridotites is expected to have occurred at much lower temperature because mantle-derived BMS at Lherz are several orders of magnitude poorer in Pt + Pd + Te (<100 ppm; Table 3). For such low contents of Pt + Pd + Te, Pt–Pd bismuthotellurides likely precipitated at sub-solidus temperature of the BMS assemblage from the very last Cu-sulfide melt fractions which should be the most Pt–Pd–Te-enriched. Note that the Te content recorded in the sulfides is that expected for equilibration temperature of ca. 200 °C (C. Ballhaus, personal communication).

Although moderately compatible in Cu-rich sulfides (chalcopyrite, cubanite; Ballhaus and Sylvester, 2000; Lorand and Alard, 2001; Luguet et al., 2004), Pd can enter pentlandite at all temperatures Thus, there is very little room for pentlandite to exsolve Pd-rich minerals. Alternatively, palladium bismuthotellurides associated with pentlandite in Pyrenean peridotites may be direct precipitation products from vapor at T < 700 °C (Gervilla and Kojojen, 2002). Likewise, not all Pt bismuthotellurides can be interpreted as direct crystallization products from Cu-rich sulfide melts. For instance, Fig. 5B and 5G provide evidence that some Pt-tellurides nucleated directly onto laurite or Pt–Ir–Os alloys, sometimes associated with hydrous silicates and Pt-arsenides. Such assemblages point to local accumulation of volatile elements (Te, Bi, As) by the refertilization process. Separate evidence is provided by lithophile trace element patterns and disseminated Ti-pargasite in Lherz and Freychinède herzolites (Fabrèi et al., 1991; Le Roux et al., 2007).

5.3. Laurite and Pt–Ir–Os alloys: refractory PGMs tracking the 2 Ga-old harzburgitic protolith inside Pyrenean herzolites

Unlike Pt–Pd–Te–Bi phases, laurite and BMS are not cogenetic since their modal abundance are negatively correlated (cf. Fig. 3). Euhedrally shaped laurite is usually interpreted as direct crystallization product from S-bearing, sulfide-undersaturated silicate melts (Augé, 1988; Brenan and Andrews, 2001; Andrews and Brenan, 2002; Bockrath et al., 2004b). Such melts may form in a mantle piece undergoing increasing degree of partial melting once the ultimate BMS fractions (compositionally close to Fe–Ni monosulfides–Mss) are dissolved into the silicate melt. At Lherz, Luguet et al. (2007) demonstrated that the whole-rock PGE budget of the 2 Ga-old S-free harzburgites is effectively hosted in discrete PGM of the laurite-erlichmanite series, Pt–Ir–Os rich alloys and complex Cu–Pt sulfides. Thus, laurite crystals now disseminated inside herzolites are interpreted as relics from this lithospheric protolith. Our interpretation is supported by BMS-laurite textural relationships, namely intermediate stages of entrapment by pentlandite, from external laurite granules simply attached to pentlandite by one crystal face to fully enclosed cubes. Likewise, our interpretation does account pretty well for the laurite crystals that are pasted on Cp or Pn–Pd intergrowths (e.g. Fig. 5C) because Ru (like Os and Ir) is not soluble in Cp and Iss-phases nor within their high-temperature precursor (i.e. Cu-rich sulfide melt, Li et al., 1996; Lorand and Alard, 2001). “Lithospheric” PGMs were mechanically collected by droplets of magmatic sulfide melt during rejuvenation reactions that refertilized the harzburgitic protolith. A preferential distribution within the grain boundary network of the lithospheric protolith (Luguet et al., 2007) likely helped “lithospheric” PGMs to be captured by herzolitic BMS. Plastic deformations coeval to the refertilization event (Le Roux et al., 2008) also played a role, as suggested by abundant PGMs in the highly deformed peridotites. At 1100 °C, the BMS were molten to partially molten, which likely enhanced their mechanical dispersion among silicate neoblasts, generating the nice wetting figures of Fig. 2.

The great similarity between Pt–Ir–Os alloys and laurite as regard their textural relationships and their associations with BMS grains argue for a similar origin (cf. Lorand et al., 2008b). Both coexist in BMS-free harzburgites (Luguet et al., 2007) and Pt–Ir–Os alloys are high-temperature phases (>1100 °C) in the Fe–Pt–Ir–S system (Fleet and Stone, 1991; Cabri et al., 1996). Ruthenium-poor, Ir + Os-rich alloy and laurite coexist stably at 1100 °C in the phase equilibrium data of
Andrews and Brenan (2002). Pt–Ir–Os alloy modal abundances vary irrespective of whole-rock S contents (cf. Fig. 3). One may speculate that lithospheric Pt–Ir–Os alloys, once trapped inside lherzolites, were not eliminated by the refertilization process because Pt is poorly soluble within Mss. Note that, although experimental data relevant to conditions of the upper mantle precludes definite answer, Perego-Odova et al. (2004) reported Mss + Cu–Ni sulfide melt saturated in Pt–Ir alloys at 1000 °C for bulk Pt contents of similar order of magnitude as the bulk concentrations estimated for Lherz/Freychinède sulfides (Table 3). Platinum systematically forms its own alloy phases in metal-rich (<50 at.% S) BMS assemblages of the Cu–Fe–Ni–S system over a wide range of temperature (Makovicky, 2002).

The decrease of laurite modal abundance with increase of BMS modal abundances in Fig. 3 most probably indicate dissolution of lithospheric crystals inside metasomatic sulfide melts. This is not surprising because 1) laurite and sulfide melts can coexist over a very restricted range of sulfur fugacity (Andrews and Brenan, 2002; Bockrath et al., 2004b; see also Fig. 5 in Luguet et al., 2007) b) Theoretical BMS phase calculated from whole-rock PGE and S analyses (Table 3) are low in Os, Ir, Ru and Rh compared with the solubility of the corresponding elements in pentlandite. Another evidence for laurite dissolution inside the BMS is provided by positive Ru anomalies in the chondrite-normalized PGE patterns of some pentlandite (Fig. 6) with Os/Ir, Ru/Os and Rh/Ir ≫ CI-chondritic ratios (Fig. 7). Nugget effects in those pentlandite grains are ruled out by the lack of coupled peaks in the signal of Ru + Os + Ir in time-resolved spectra. Each lherzolite analysed in the present study shows such Ru-rich BMS which are most abundant in 71-339, the richest in laurite. The simplest explanation is that Ru, Os and Ir were not able to rehomogenise their concentrations. Pyrenean lherzolites were quickly uplifted as small-sized bodies (~1 km³) and cooled at 600 °C within crustal country rocks within less than 1 Ma (Fabriès et al., 1998). It is worth noting that FON-B 93 is devoid of laurite, although it is as rich in PCMs as the richest samples at Lherz and Freychinède. We may speculate that laurite totally dissolved inside the BMS owing to the longer period of annealing of silicate assemblages at mantle temperatures that generated the secondary protogranular microtexture of Fontète Rouge lherzolites (Fabriès et al., 1991).

A set of peculiar conditions allowed the laurite to be locally preserved. Epitaxial growth of sulfide melts on pre-existing laurites can account for much of the laurite-BMS microtextures in Fig. 5. A similar explanation also holds true for those Pt–Ir–Os alloys which are not enclosed, just attached on small-sized Pn blebs. Plastic deformations in Pyrenean peridotites ended at rather low temperatures (~500 °C). This is the likely reason why laurite was found to be attached to the smallest BMS blebs. Sharing only one or two crystalline faces with BMS grain, those grains suffered limited diffusion of Ru, Os and Ir with the BMS.

### 5.4. Implications for the PGE budget of Pyrenean peridotites

Not only the BMS phases but also PCM micronuggets must be taken into account to calculate the PGE budget of orogenic fertile lherzolites. Laurite is a good candidate for fully equilibrating the whole-rock budget of Ru, coupled with Pt–Ir–Os alloys for Os and Ir. In addition to an overall Pt deficit (75–99%) that reflects the abundance of Pt-rich PCMs, the measured BMS compositions in the cpx-rich harzburgites and lherzolites that are rich in PCMs and poor in Pt do not balance the whole-rock PGE budget for Os, Ru, Ir and Rh (Table 3). Of course, the unaccounted fraction decreases from 71–322 to 82–4 and 04Lh08 as BMS modal abundance increases. Sample 04Lh08, as rich in BMS as UB-N (145 vs. 141–133 ppm S; Lorand et al., 2008a) displays unaccounted fractions of Os and Ir not residing inside BMS of similar extent as this rock standard (30 ± 20% Os and 40 ± 20% Ir; Meisel et al., 2003). By contrast, as suggested by FONB-93 (Lorand et al., 2008b), fertile lherzolites, which are the most-enriched in BMS, do not display such a deficit. Calculated and measured contents of Os, Ir and Rh agree at 1 sigma level; the rather large uncertainties on measured compositions preclude a precise estimate of the contribution of PCMs.

Unlike Os and Ir, the concentrations of Ru measured in BMS of fertile lherzolites display rather a constant deficit of ca. 50% compared to calculated concentrations. This obviously tracks laurite, although...
this sulfide, preferentially adhering to the smallest BMS blebs, has not been detected in all the analysed samples. A simple calculation based on sample 71 339 (4 ± 2 perfectly cubic laurite crystals, each representing arbitrarily 8 µm³ by volume per 30 µm-thick standard sized polished thin section) allows the volume of laurite to be estimated at 1 ± 0.3 × 10⁻⁸ cm³, which transposes into 2 ± 1 × 10⁻⁸ g/cm³ (density = 6.4). EDS spectra indicate higher Ru contents than Os and much lower Ir abundances relative to Ru and Os in hertzolitic laurites. Assuming Ru content of 40 ± 10 wt.%, laurite may account for 0.5–1.5 ppb Ru, i.e., up to 25% of the whole-rock budget of Ru of a hertzolite with a PGM-like PGE composition (7.1 ppb Ru). That contribution is obviously underestimated compared to mass balance calculations of Table 3 because 1) volume estimate of microminerals is prone to considerable error, 2) not all of the laurite crystals were intercepted by the thin sections of 71 339 and 3) in-situ LAM-ICPMS analyses provide evidence for one laurite population already dissolved into the BMS phase.

6. Conclusions

Pyrenean hertzolites clearly contain two generations of PGMs (a) refractory minerals (laurite-erlichmanite series, Pt–Ir–Os alloys) inherited from ancient highly depleted harzburgitic protolith and (b) “low-temperature” bismuthotelurides and arsenides/sulfarsenides, intimately associated with Pd-rich metamasic BMS, indicators of lithosphere refertilization process, in agreement with Le Roux et al. (2007, 2008, 2009) model. Such platinum-group minerals have been identified in hertzolites from several orogenic locations, all displaying unambiguous petrological evidence of magma refertilization processes of formerly depleted lithosphere (e.g. Corsican plagioclase hertzolites (Sudbury Igneous Complex, Sudbury, Canada): implications for the formation of the reef. J. Petrol. 48, 1569

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References

