Mineralogical and geochemical constraints on the shallow origin, ancient veining, and multi-stage modification of the Lherz peridotite

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Received 29 November 2010; accepted in revised form 25 July 2011; available online 31 July 2011

Abstract

New major- and trace-element data of bulk-rocks and constituent minerals, and whole-rock Re–Os isotopic compositions of samples from the Lherz Massif, French Pyrenees, reveal complex petrological relationships between the dominant lithologies of lherzolite ± olivine-websterite and harzburgite. The Lherz peridotite body contains elongate, foliation parallel, lithological strips of harzburgite, lherzolite, and olivine-websterite cross-cut by later veins of hornblende-bearing pyroxenites. Peridotite lithologies are markedly bimodal, with a clear compositional gap between harzburgites and lherzolites ± olivine-websterite. Bulk-rock and mineral major-element oxide (Mg–Fe–Si–Cr) compositions show that harzburgites are highly-depleted and result from \(\sim20-25\) wt.% melt extraction at pressures <2 GPa. Incompatible and moderately-compatible trace-element abundances of hornblendite-free harzburgites are analogous to some mantle-wedge peridotites. In contrast, lherzolites ± olivine-websterite overlap estimates of primitive mantle composition, yet these materials are composite samples that represent physical mixtures of residual lherzolites and clinopyroxene dominated cumulates equilibrated with a LREE-enriched tholeiitic melt. Trace-element compositions of harzburgite, and some lherzolite bulk-rocks and pyroxenes have been modified by; (1) wide-spread interaction with a low-volume LREE-enriched melt +/− fluid that has disturbed highly-incompatible elements (e.g., LREEs, Zr) without enrichment of alkali- and Ti-contents; and (2) intrusion of relatively recent, small-volume, hornblende-forming, basanitic melts linked to modal and cryptic metasomatism resulting in whole-rock and pyroxene Ti, Na and MREE enrichment.

Rhenium-Os isotope systematics of Lherz samples are also compositionally bimodal; lherzolites ± olivine-websterite have chondritic to suprachondritic \(^{187}\text{Os}/^{188}\text{Os}\) and \(^{187}\text{Re}/^{188}\text{Os}\) values that overlap the range reported for Earth’s primitive upper mantle, whereas harzburgites have sub-chondritic \(^{187}\text{Os}/^{188}\text{Os}\) and \(^{187}\text{Re}/^{188}\text{Os}\) values. Various Os-model age calculations indicate that harzburgites, lherzolites, and olivine-websterites have been isolated from convective homogenisation since the Meso-Proterozoic and this broadly coincides with the time of melt extraction controlled by harzburgite Os-isotope compositions. The association between harzburgites resulting from melting in mantle-wedge environments and Os-rich trace-phases (laurite–erlichmanite sulphides and Pt–Os–Ir-alloys) suggests that a significant portion of persistent refractory anomalies in the present-day convecting mantle of Earth may be linked to ancient large-scale melting events related to wide-spread subduction-zone processing.

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1. INTRODUCTION

The origin of orogenic massifs (c.f. Den Tex, 1969; Wylie, 1969), including the Lherz peridotite, has been the subject of much debate and it has been suggested that these layered assemblages of peridotite and pyroxenite may rep-
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from cross-cutting veins are isotopically enriched with high $^{87}$Sr/$^{86}$Sr (0.70475 ± 4), high $^{87}$Rb/$^{86}$Sr (~0.0075), and contrast to lherzolites that commonly display low $^{87}$Sr/$^{86}$Sr (0.70202 ± 2 to 0.70274 ± 4), low $^{87}$Rb/$^{86}$Sr (0.0011–0.0042), and high $^{238}$U/$^{206}$Pb (7.2 ± 11.9); these isotopic characteristics are not the result of melt extraction processes alone (Downes et al., 1991; Le Roux et al., 2009).

Two contrasting petrogenetic models may account for the compositional diversity of the Lherz massif; (1) harzburgites and lherzolites may result from variable degrees of ancient melt extraction, and isotope systems based on incompatible lithophile-elements may record later events linked to thermal perturbation and/or incompatible-element modification by moderate amounts of exotic melts and/or fluids (e.g., Burnham et al., 1998; Henry et al., 1998); or (2) Le Roux et al. (2007, 2008, 2009) recently proposed that the peridotite–pyroxenite assemblage of Lherz could reflect refertilisation of ancient depleted peridotites by substantial volumes of percolating basaltic melt (30–60 wt.% websterite, where these authors view websterites as frozen melt-fronts) during the Variscan orogeny. It is important to distinguish between these models as recent suggestions of Variscan-age igneous refertilisation may cast doubt on the significance of osmium model-age determinations for the Lherz massif and other global peridotite suites. If correct, the model proposed by Le Roux et al. (2007, 2008, 2009) has important geodynamic implications if mineralogically fertile LREE-depleted lherzolites are secondary products, and if large-volumes of basaltic melt can ascend through mantle lithosphere by widespread percolative flow (defined herein as igneous refertilisation) that; (1) crystallises substantial amounts of secondary clinopyroxene ± spinel ± sulphide ± amphibole; and (2) is characterised by pronounced fractionation of trace-elements at a chromatographic melt-front (c.f. Verniers et al., 1997).

In this study we report new field and petrographic characteristics, mineral and bulk-rock major-, minor-, and trace-element abundances, and whole-rock Re–Os concentrations and isotopic compositions of adjacent harzburgite and lherzolite bodies (± olivine-websterite) at two sample traverses within the Lherz massif. We demonstrate that the peridotites and (diopside-bearing) olivine-websterites of the Lherz massif were created in low-pressure environments (spinel–facies) where melt migration was dominated by channel-flow during the Proterozoic. In addition, we show that; (1) magnesian harzburgites with low-Ti clinopyroxenes, analogous to some mantle-wedge peridotites, may result from low-pressure (~<2 GPa) melting in the presence of fluid; (2) incompatible-element abundances for this sample suite are decoupled from major-element and Os-isotope systematics, recording two distinct post-differentiation metasomatic events linked to; (a) wide-spread interaction with a LREE-enriched melt +/− fluid; and (b) short-length-scale modal and cryptic modification adjacent to hornblende-veinlets. These results cast serious doubt on the igneous refertilisation model of Le Roux et al. (2007, 2008, 2009), and indicate that the oldest portions of the Lherz massif represent tectonically juxtaposed lithologies that formed in a mantle-wedge environment.

As a large, well exposed, relatively fresh expanse of peridotite that can be subjected to field investigations on all length scales up to 1 km$^2$ (e.g., Conquéré and Fabriès, 1984; Bodinier et al., 1988; Fabriès et al., 2001; Le Roux et al., 2007) the Lherz massif has occupied a prominent position in debates concerning mantle evolution. Lherz is one of the few exposed mantle-wedge massifs (e.g., Reisberg and Lorand, 1995) that formed in a mantle-wedge environment.

The Re–Os isotope system is widely considered to record high-temperature processes (e.g., Shirey and Walker, 1998; Carlson, 2005; Pearson et al., 2007; Carlson et al., 2008), and Re–Os isotopic compositions of peridotites have been used to estimate the timing of major mantle differentiation events; methods of applying this tool to obtain osmium-model ages (Alumino-chron and Sulphur-chron approaches) were founded on studies of the Lherz peridotite and other Ariège-group massifs (e.g., Reisberg and Lorand, 1995; Burnham et al., 1998). These Os-dating methods have been applied to a number of other massif peridotite, ophiolite, abyssal peridotite, and xenolith suites (e.g., Ronda and Horoman massifs, Reisberg et al., 1991; Saal et al., 2001; Southeast Australian Xenoliths, Handler et al., 1997; North China Xenoliths, Gao et al., 2002; Liu et al., 2010, 2011; Gakkel Ridge peridotites, Liu et al., 2008) where mantle depletion ages have tentatively been linked to periods of significant crustal generation and lithosphere stabilisation (c.f. review by Rudnick and Walker, 2009).

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2. FIELD, PETROGRAPHIC AND MINERALOGICAL CHARACTERISTICS

2.1. Field constraints

The Lherz peridotite body is a layered ultramafic sequence dominated by foliated peridotite in which the broadly NE-SW striking fabric (Fig. 1b) is defined by elongate silicate grains (olivine + pyroxene). Concordant harzburgites form subordinate tabular features in direct contact with lherzolite lithologies ± olivine-websterite. Some lherzolites contain bands of olivine-websterite (up to 10 cm wide) that parallel the foliation plane with a broad NE–SW strike. Field relationships indicate that the banded series of harzburgite, lherzolite, and concordant olivine-websterite is old relative to volumetrically minor anhydrous layered-pyroxenite (± garnet) sequences (up to 4 m thick; Bodinier et al., 1987a) that cross-cut the peridotite foliation at angles of ~20° (Conquéré and Fabriès, 1984; Fabriès et al., 2001). In addition, Sautter and Fabriès (1990) indicated that the peridotite assemblage, olivine-websterite bands, and layered anhydrous–pyroxenites are isoclinally folded within Ariège-group peridotite bodies. Late-stage intrusive features dated at ~100 Ma (e.g., Montigny et al., 1986; Henry et al., 1998) include amphibole-bearing pyroxenites and hornblendite-veins that cross-cut the dominant foliation within spinel peridotites at angles of ~30° (Conquéré and Fabriès, 1984; Fabriès et al., 2001). More recent studies by Le Roux et al. (2007, 2008, 2009) suggested an alternative view in which the contacts between harzburgites and lherzolites are convoluted and the foliation within harzburgites is overprinted by later mineral growth (secondary pyroxene ± spinel ± amphibole ± sulphide) linked to the generation of secondary lherzolites during a pervasive igneous refertilisation process.
In this study, two sample traverses were undertaken across contacts between harzburgite and lherzolite bodies that contain contrasting abundances of pyroxenite. Site A contains a high pyroxenite abundance evident in the form of numerous olivine-websterite bands (1.5–8 cm wide) within the lherzolite body, and this traverse coincides with site 4 of Lorand et al. (2010). Site B, which corresponds to traverse 2 of Le Roux et al. (2007, 2008, 2009) and site 2 of Lorand et al. (2010), has a low pyroxenite abundance with no clear exposure of olivine-websterite bands (where bands are continuous features distinct from websteritic pods <30 cm in length) in the lherzolite body over the sampling scale of this work. In contrast to Le Roux et al. (2007, 2008, 2009) and Lorand et al. (2010) we observed hornblendite–veinlets (<2 cm in width, Fig. A1 of Appendix A) in several samples proximal to the harzburgite–lherzolite contact at site B. Le Roux et al. (2007) suggested that harzburgites record a foliation of N40–60°E that is over-printed by a later and more steeply dipping foliation in lherzolites. Field observations confirm that the foliation of harzburgites and lherzolites proximal to the compositional boundary at site B is weak, and that the foliation deviates from the N40–60°E orientation that is dominant across the massif. Site A is structurally distinct from site B (Fig. A2, Appendix A). At site A, the foliation within the harzburgite and banded-lherzolite body is coincident and conforms to the N40–60°E plane observed at many outcrops across this massif. Olivine-websterite bands within the lherzolite body at site A are generally concordant with the foliation defined by elongate silicates of the adjacent peridotite. In addition, the contact between harzburgite and lherzolite at sites A and B is sharp (at the 10 cm and thin section scale), and these observations are consistent with previous field studies and structural maps of Lherz in which harzburgite and lherzolite lithologies represent elongate lithological strips (e.g., Conquére and Fabriès, 1984; Fabriès et al., 2001 and references therein) juxtaposed during plastic deformation (e.g., Fig. 2 of Sautton and Fabriès, 1990).

2.2. Petrographic features

Samples collected during this study are up to 20 × 30 × 20 cm in size and are heterogeneous at the hand-specimen scale. All studied samples are coarse-grained peridotites and olivine-websterites (silicates are typically 5–10 mm at the long axis), dominated by olivine, orthopyroxene, clinopyroxene, spinel, minor amphibole, and minor sulphide in an interlocking crystalline matrix with a porphyroclastic texture (porphyroclasts are up to 25 mm at their long axis). Many samples from site A and several samples from site B are hybrid formations of peridotite ± olivine-websterite (bands and pods), and these composite samples are distinct from relatively homogeneous, mineralogically fertile, peridotites that have been incorporated into previous studies that addressed the composition of Earth’s primitive mantle (e.g., McDonough and Sun, 1995). Olivine, orthopyroxene, and clinopyroxene crystals are elongate and show a preferred alignment, defining a clear foliation within the samples. Isolated areas (generally <3 mm wide) of later crystallised pyroxene ± spinel ± sulphide ± minor amphibole are volumetrically minor (generally <5 vol.%, particularly in samples distal from cross-cutting hornblendite veinlets). Similar features have been identified in previous petrographic and mineralogical studies of the Lherz peridotites (e.g., Lorand, 1989, 1991; Woodland, 1992; Woodland et al., 1996). Minor trails (<0.5 mm wide) of spinel parallel the penetrative foliation in some places, but are often inclined to it, consistent with observations by Woodland (1992), and Woodland et al. (1996). All studied specimens have experienced relatively low degrees of serpentinisation.
2.3. Mineralogical characteristics

Major- and minor-element compositions of constituent minerals are reported with trace-element abundances of clinopyroxene in Appendix B. Porphyroclastic and matrix phases commonly cover a limited range of major-element contents, and some crystals <0.5 mm in diameter display irregular compositional zoning. In general, constituent phases of peridotites and olivine-websterites within the Lherz massif have Mg# (where Mg# = 100Mg/(Mg + Fe\text{total})) values of the order spinel < olivine < orthopyroxene < clinopyroxene.

2.3.1. Olivine and spinel compositions

Peridotites and olivine-websterites of the Lherz massif contain forsteritic olivine, with the most magnesian compositions present in harzburgites (Mg# = 91–92), and Mg# = 90–91 at sites A and B, respectively, and olivines with lower Mg# (89–90) present in lherzolites, composite-lherzolites, and olivine-websterites. Harzburgites associated with hornblende-veinlets contain olivine with Mg# values (~91) similar to those of hornblende-free harzburgites. The Mg# of olivines generally corresponds to the bulk-rock composition, and the variation of olivine mode with Mg# in several peridotites of the Lherz massif overlaps the oceanic trend of Boyd (1989); (Fig. A3 of Appendix A). In detail, several harzburgite samples from site A and B contain lower modal abundances of olivine and greater concentrations of orthopyroxene than predicted by the oceanic trend (Fig. A3, Appendix A), and only one of these samples contains visible hornblende. Nickel contents of olivines of site A and B generally range from 0.38 to 0.46 wt.% NiO, and extend to lower values (reaching 0.26 wt.% in composite-lherzolites of site A, with a maximum NiO content (0.54 wt.%) in a lherzolite spatially associated with hornblende at site B (04LH04). This range of Mg# and Ni contents is similar to those reported for in olivine-websterites and peridotites of abyssal peridotites, forearc peridotites, and ophiolite sequences, and cratonic xenoliths (e.g., Kelemen et al., 1998; O’Hara and Ishii, 1998; Suhr et al., 2003; Dick et al., 2010; Warren and Shimizu, 2010).

Several types of spinel were identified on the basis of their textural locations and major-element compositions by Woodland et al. (1996), and definitions suggested by these authors have been adopted and expanded in this work. We recognise four spinel-types: (1) P-type spinels (<1 mm) are common, occur interstitially, and are generally anhedral with dark-brown to mid-brown body colour, (2) S-type spinels have similar crystal form and textural associations to P-type spinels, but are less common and have varying body colour that is olive-green and red-brown in some cases, (3) rare G-type spinels (<0.5 mm) occur in a limited number of harzburgite samples, have olive-green body colour, and often form as isolated crystals at olivine-olivine contacts or adjacent to elongate orthopyroxene, and (4) C-type spinels (0.5–1 mm) occur with clinopyroxene in symplectic clusters and have irregularly varying body colour ranging from olive-green to dark-brown. In general, spinels are of chromite to Al-chromite composition and have major-element characteristics similar
2.3.2. Pyroxene and amphibole compositions

The studied samples contain diopside and enstatite covering a range of jadeite contents (<1 to 14.3 mol.%). Clinopyroxene compositions can be divided into three groups on the basis of their major-element contents. Two clinopyroxene groups dominate the studied samples and these fall on trend 1 of Supplementary Fig. A4 (Appendix A); hornblende-free harzburgites contain group-1 clinopyroxenes with the lowest Na₂O and highest Al₂O₃ contents of all studied diopsides, and group-2 pyroxenes hosted by hornblende-free lherzolites and olivine-websterites have moderate Na₂O and Al₂O₃ contents. Lesser amounts of Group-3 clinopyroxenes are present in the studied samples, and these are found in hornblende-bearing harzburgites and hornblende-free harzburgites that crop out proximal to the compositional boundary at sites A and B; group-3 diopsides have higher Na₂O contents at equivalent Al₂O₃ abundances (trend 2 of Fig. A4, Appendix A) compared to clinopyroxene groups 1 and 2. Pyroxenes with relatively high Na₂O abundances also have high Cr₂O₃ and lower CaO contents at a given Al₂O₃. Group-3 clinopyroxenes from each sample site differ when Ti-abundances are compared (Appendix B). Group-3 clinopyroxenes of site B, often associated with visible hornblende, contain up to 1.2 wt.% TiO₂, and are analogous to clinopyroxenes previously reported for Lherz peridotites that; (1) crop out adjacent to amphibole-pyroxenites (Woodland et al., 1996); (2) are linked to the refertilisation trend defined by Le Roux et al. (2007). Group-3 clinopyroxenes of site A (samples 04LH34A and 04LH35) have much lower Ti-contents (<150 ppm, Appendix B) than abyssal peridotite clinopyroxenes (Ti > 240 ppm; Dick et al., 2010; Warren and Shimizu, 2010) and are analogous to low-Ti clinopyroxenes of subduction-zone peridotites (e.g., Ti <150 ppm; Parkinson et al., 1992; Bizimis et al., 2000).

Harzburgites of the Lherz massif contain minor amounts of interstitial amphibole and previous studies suggested that pargasitic compositions are common (e.g., Downes et al., 1991; Fabriès et al., 1991). Lherzolites, composite-lherzolites, and olivine-websterites contain greater abundances of interstitial amphibole than harzburgites, and distinct compositional groups are present at each sample site. Amphiboles of site A lherzolites ± olivine-websterites are generally sodic and of eckermannite composition (Appendix B). In contrast, amphiboles of site B harzburgites and lherzolites ± hornblende are generally calcic with pargasitic to Mg-gedrite compositions. Amphiboles present in hornblende-veinlets are kaersutic, and are optically and compositionally analogous to amphiboles reported in previous studies of hornblende lithologies within the Lherz massif (e.g., McPherson et al., 1996; Fabriès et al., 2001; Lorand and Gregoire, 2010).

2.3.3. Geothermometry

Equilibration temperatures calculated from core compositions of pyroxene, olivine, and spinel phases in a number of textural locations (e.g., porphyroclasts, typical matrix, and pyroxene-spinel symplectites) are reported in Appendix B, and are generally ~800–900 °C, ~720–900 °C, and ~650–900 °C for two-pyroxy, orthopyroxene-spinel, and olivine-spinel thermometry, respectively. This range of equilibration temperatures is similar to those reported in earlier studies of Ca–Al–Fe–Mg thermometry within the Ariège-group peridotites (e.g., Conquéré and Fabriès, 1984), and reflects cooling to lithospheric conditions substantially below; (1) the peridotite solidus (c.f. Hirschmann, 2000; Wasylenki et al., 2003; Herzberg, 2004; for a compilation of anhydrous and H₂O under-saturated solidus curves); and (2) the potential temperature thought to be typical of MORB mantle (e.g., 1280 °C; McKenzie and Bickle, 1988). Conquéré and Fabriès (1984) studied a number of Ariège-group peridotite bodies that crop out at different points along the North Pyrenean Metamorphic Zone and suggested that two distinct episodes of subsolidus re-equilibration are recorded across this region. The first re-equilibration episode proposed by these authors, R₁–D₁, has been linked to peridotites with coarse-granular textures (e.g., Fontète Rouge peridotites), and may reflect cooling to temperatures of 900–1000 °C at pressures of 12–15 kbar. The second re-equilibration event, R₂–D₂, is associated with porphyroclastic textures (like those reported for the Lherz massif), development of a penetrative foliation, formation of cm-thick ultra-mylonite bands in some places (Avé Lallement, 1967), and records equilibration extending to lower temperatures and pressures (down to ~750 °C and 8–13 kbar; Vétèl et al., 1988). The second of these regionally recognised mantle re-equilibration events is consistent with thermometric results reported here.

3. WHOLE-ROCK AND PYROXENE CHEMISTRY

3.1. Bulk-rock major-element, Cr, and Ni abundances

The studied sample suite displays highly systematic variations in major-element compositions (Fig. 2 and Appendix A) with pronounced negative correlations between MgO (29.5–46.4 wt.%) and CaO (0.34–7.53 wt.%), Al₂O₃ (0.47–7.80 wt.%), Na₂O (<0.05–0.65 wt.%) and SiO₂ (42.9–
46.8 wt.%). By contrast, abundances of MgO and FeO are not well correlated (not shown) in that lherzolites and harzburgites covering a range of MgO contain up to 8.32 wt.% FeO, while the minimum harzburgite FeO content is 7.67 wt.%, and composite-lherzolites and olivine-websterites extend to lower FeO values (6.33 wt.%). This range of values coincides with those reported in previous studies of the Lherz massif (e.g., Bodinier et al., 1988; Burnham et al., 1998), and linear correlations between bulk-rock CaO, Al2O3, MgO, and SiO2 contents are a common feature of peridotite–pyroxenite assemblages in other ultramafic bodies such as Beni-Bousera, Horoman, and Ronda (e.g., Frey et al., 1985; Bodinier and Godard, 2003). This range of compositions overlaps estimated compositions of BSE (e.g., Figs. 2 and 3) and depleted MORB mantle (DMM; Workman and Hart, 2006).

In more detail, the studied sample suite is broadly bimodal with harzburgite MgO abundances generally between 45 and 47 wt.%, whereas lherzolites, composite-lherzolites and olivine-websterites contain <40 wt.% MgO. These harzburgites have low Al2O3 (<1 wt.%), CaO (<1 wt.%), and high Ni contents (2142–2379 ppm) and Mg# (91.7–92.1), consistent with >70 wt.% olivine and <5 wt.% clinopyroxene resulting from ~20–25 wt.% melt removal (Appendix A). In contrast, lherzolites ± olivine-websterite bands have higher Al2O3 (1.5–5.8 wt.%), CaO (2.0–5.6 wt.%), and lower MgO (34–43 wt.%), Ni (1542–1918 ppm) contents, and Mg# (90.3 to 91.6) corresponding to higher pyroxene abundances. Olivine-websterite bands have the highest Al2O3 (6.6–7.8 wt.%), CaO (6.9–7.5 wt.%), lower MgO (31–29 wt.%), Mg# (90.2–91.5) within the range of enclosing lherzolites, and the lowest Ni abundances (1412–1381 ppm) consistent with >60 wt.% pyroxene and <30 wt.% olivine. The majority of studied lherzolites ± olivine-websterite bands are composite samples with Al2O3 values in excess of primitive mantle estimates, and these specimens are not simple residues of melt extraction.

Despite the strong systematic co-variations in abundances of many major-element oxides (e.g., Fig. 2a), there are significant differences in the major-element systematics of the two sample sites that are exemplified by plots of Mg/Si against Fe/Si, and Cr/Al against distance from the compositional boundary (Figs. 2c and 3). Harzburgite and lherzolite samples generally have Cr/Al values that define distinct groups related to each lithology. Harzburgites...
commonly have high Cr/Al values that range from 0.50 to 0.85, whereas lherzolites, composite lherzolites, and olivine-websterites generally have Cr/Al values <0.20. A number of samples at site B have Cr/Al values that are intermediate (0.28–0.45) between harzburgite and lherzolite end-members; these generally crop out close (<1.5 m) to the compositional boundary between adjacent lherzolite and harzburgite bodies at site B. Samples with intermediate Cr/Al contain visible, or crop out in close proximity to mm- to cm-scale hornblendite veins. Samples associated with hornblendite-veinlets at site B have Mg#'s that are intermediate between; (1) distal harzburgite and lherzolite samples of site B; and (2) all samples of site A.

On the basis of Mg–Fe–Si systematics peridotites of site A are separated into two distinct compositional groups corresponding to harzburgite and lherzolite bodies (Fig. 3). Harzburgites define a tightly-clustered group with a narrow range of Mg/Si (1.298–1.326) and Fe/Si values (0.286–0.298). Lherzolites and olivine-websterites of site A define a striking linear trend with Mg/Si varying from 0.809 to 1.099 as Fe/Si increases from 0.224 to 0.309. This trend coincides with the estimated composition of BSE given by McDonough and Sun (1995), and the DMM-value of Workman and Hart (2006). In contrast, peridotites of site B do not show such a clear division between lherzolites and harzburgites and cover a narrower range of Fe/Si values. Harzburgites define a clustered group with Fe/Si values between 0.298 and 0.314 and Mg/Si values of 1.341–1.389. Site B lherzolites cover a range of Fe/Si and Mg/Si values (0.273–0.314 and 1.031–1.271, respectively) defining an elongate field sub-parallel to the linear correlation reported for the websterite-banded lherzolite body of site A (Fig. 3). Taken together, the harzburgite samples of site A and site B describe an elongate field that is sub-parallel to the lherzolite field of site B.

3.2. Bulk-rock and pyroxene trace-element characteristics

Lherz peridotites (± olivine-websterite) and their constituent pyroxenes cover a range of trace-element abundances (Figs. 4 and 5, Appendices A and B), and the rare-earth-element (REE) profiles of bulk-rocks are reflected by the REE-patterns of constituent clinopyroxenes. In general, lherzolites and olivine-websterites are light-rare-earth-element (LREE) depleted and have higher abundances of heavy- and middle-rare-earth-elements (HREE and MREE) than harzburgite samples. Europium anomalies ([Eu/Eu\textsuperscript{N}]N, where [Eu\textsuperscript{N}]N = [(Gd + Sm)/2]N, and N denotes normalisation to CI-chondrite) of the studied samples are 0.44–0.74 (Appendix B), and constituent pyroxenes generally have ([Eu/Eu\textsuperscript{N}]N of 0.24–0.32; these relatively small negative values differ from positive Eu-anomalies (>1) reported for bulk-rocks and clinopyroxenes of selected ophiolite peridotites from the Eastern Central Alps (e.g.,
Hornblendite-free harzburgites of site A are characterised by U-shaped REE-patterns, and samples with the greatest degree of LREE-enrichment also have elevated chondrite-normalised U and Th relative to Ba and Nb. The trace-element systematics of peridotites at site B, differ from those of site A, and show a wide-range of REE-patterns, including convex-upward and sinusoidal shapes (e.g., Fig. 4); the latter are generally found in hornblendite-bearing rocks or spatially associated samples, whereas U-shaped REE-patterns are present in samples that lack hornblendite and have low bulk Ti-contents (<30 ppm). In general, the studied samples lack the selective enrichment of large-ion-lithophile-elements (LILE; Cs, Rb, Ba, and Sr) relative to high-field-strength-elements (HFSE; Th, U, Nb, Ta, Zr, and Hf) reported for SSZ-peridotites of the Izu–Bonin–Mariana arc sequence (Fig. 5), but hornblendite-free harzburgites have chondrite-normalised trace-element patterns similar to harzburgite xenoliths recovered from the Avacha volcano, Kamchatka arc (Ionenov, 2010).

The range of trace-element abundances in the studied bulk-rocks and clinopyroxenes is similar to the compositional range reported in previous investigations of the Lherz massif (e.g., Bodinier et al., 1988, 1990; McPherson et al., 1996; Burnham et al., 1998; Bodinier et al., 2004; Le Roux et al., 2007, 2009). No extremely depleted clinopyroxenes, analogous to that reported for harzburgite 06LI15 (REE ≤ CI-chondrite abundances; Le Roux et al., 2009) are...
present in our sample set. Bulk-rock HREE contents and ratios determined in this study overlap the range previously reported for Lherz peridotites and for peridotite and pyroxenite assemblages of other Ariège-group massifs, Ronda, Horoman, and the Beni-Bousera ultramafic complexes (Fig. 6a).

Trace-element partition coefficients between co-existing clinopyroxene (Kd\textsubscript{CPX/OPX}) and orthopyroxene (Kd\textsubscript{CPX/OPX}) phases are broadly analogous to those reported in previous studies of mantle peridotites (e.g., Stosch, 1982; Bodinier et al., 1988; Eggins et al., 1998; Witt-Eickschen and O’Neill, 2005; Lee et al., 2007; Harvey et al., 2010; Appendix B). Absolute values of REE Kd\textsubscript{CPX/OPX} are relatively high in the studied sample suite that has equilibration temperatures of \( T < 800 \) °C or less. The elevated REE Kd\textsubscript{CPX/OPX} values of Lherz samples with lower equilibration temperatures than reported for several xenolith suites (refer to Appendix B) probably reflect the temperature dependence of subsolidus REE redistribution that is thought to be linked to Ca-exchange between clinopyroxene and orthopyroxene during cooling (e.g., Witt-Eickschen and O’Neill, 2005 and references therein), and this is the subject of ongoing study.

Fig. 6. Moderately-incompatible (Dy, Yb, V), incompatible (Ti), and highly incompatible (Zr) trace-element compositions of bulk-rocks (Bulk; (a) and (b) and constituent clinopyroxenes (CPX; (c) and (d) Bulk-rock models of spinel- (Sp) and garnet- (Gt) facies fractional melting assume a starting composition equivalent to that of primitive mantle (PUM; McDonough and Sun, 1995) and incorporate melting modes and partition coefficients reported by Johnson et al. (1990) that are relevant for anhydrous conditions. These melting curves reflect dynamic melting in which a critical porosity retains 1% of the melt in all residues (after McKenzie, 1985). The melting modes of Kinzler (1997) are used in our calculations. The blue curve in (a) describes compositions expected for melting residues produced under hydrous conditions in the mantle-wedge where HREEs are expected to be more incompatible (Gaetani et al., 2003; McDade et al., 2003). Vanadium is multi-valent on Earth, occurring as V\textsuperscript{3+}, V\textsuperscript{4+}, and V\textsuperscript{5+}; models of bulk-rock abundances resulting from variable degrees of fractional melting are redox sensitive and are shown over a range of oxidation conditions (FMQ – 1 to FMQ + 1; after Parkinson and Pearce, 1998). Data fields delineate the range of compositions reported for spinel-bearing peridotites devoid of garnet ± plagioclase (Bodinier et al., 1987b; Bodinier et al., 1988; Fabriès et al., 1988; Bodinier et al. 1990; McPherson et al., 1996; Van der Wal and Bodinier, 1996; Burnham et al., 1998; Fabriès et al., 1998; Parkinson and Pearce, 1998; Garrido et al., 2000; Lenoir et al., 2000, 2001; Downes, 2001; Beccaluva et al., 2004; Bianchini et al., 2007; Ionov, 2010), and clinopyroxene compositions determined by in-situ methods (Parkinson et al., 1992; Bizimis et al., 2000; Johnson et al., 1990; Johnson and Dick, 1992; Warren and Shimizu, 2010). SSZ = supra-subduction zone, MOR = mid-ocean ridge. Hb-hazburgite = hornblendite-bearing harzburgite, Hb-Lherzolite = hornblendite-bearing lherzolite, OI-Websterite = olivine-websterite, and C-Lherzolite = composite-lherzolite, see the main text for details. FMM = fertile MORB mantle (Pearce and Parkinson, 1993), DMM = depleted MORB mantle (Workman and Hart, 2006).
3.3. Bulk-rock S, Cu, Re and Os concentrations and Re–Os isotope compositions

Bulk-rock S, Cu, Re, and Os abundances and Re–Os isotopic compositions generally fall into distinct compositional groups with no clear gradation across the compositional boundary between harzburgites and lherzolites at sites A and B (Fig. 7). Harzburgites have low bulk S and Cu contents (35–52 ppm and 1.12–2.90 ppm, respectively), whereas lherzolites and composite-lherzolites have high S and Cu contents (163–415 ppm and 16.2–42.1 ppm, respectively). Olivine-websterites measured in this study have S contents (334 ppm; 04LH38) within the range observed in spatially associated lherzolites, but higher Cu concentrations (77.6 ppm; 04LH14A) than adjacent peridotites. Sulphur and Re abundances define broad negative correlations with increasing bulk-MgO content (Fig. A8 of Appendix A), and this range of values coincides with those previously reported for the Lherz peridotite body (Reisberg and Lorand, 1995; Burnham et al., 1998), passing close to estimates of primitive mantle composition (Appendices A and B). A limited number of samples (04LH07A, 04LH37B) have relatively high S contents at a given MgO concentration, and these rocks also have elevated Re contents. The olivine-websterite analysed in this work (04LH38) has low S and Re abundances when compared to the dominant negative correlation between these elements and bulk-MgO (Fig. A8, Appendix A). Harzburgites generally have high osmium contents (4012–5312 ppt) with few Lherz harzburgites containing <4100 ppt (an exception includes 04LH34A of site A with 3017 ppt Os). Lherzolites and composite-lherzolites have Os concentrations that generally range from 3624 to 4112 ppt, and these lherzolites rarely have Os abundances in excess of 4100 ppt. Lherzolite 04LH07A, associated with hornblendite-veinlets and characterised by relatively high Re and S abundances, has the highest Os content (4538 ppt) of the studied sample suite. Olivine-websterite 04LH38 has the lowest osmium concentration (2830 ppt) of all studied samples, and this value is significantly greater than Os concentrations generally reported for basaltic materials (e.g., 1–50 ppt range of MORB; Shirey and Walker, 1998). Measured Os abundances in this sample suite coincide with the range of values reported in other investigations of Lherz peridotites, and these data do not define a strong positive correlation with bulk-MgO (Appendices A and B).

Harzburgites generally have low 187Re/188Os (0.023 ± 0.002 to 0.066 ± 0.007) and sub-chondritic 185Os/188Os values that are within uncertainty of one another (≈0.117; Fig. 7 and Appendix B), and higher 185Os/188Os values than reported for the 4 low-S harzburgites studied by Luguet et al. (2007). Few studied harzburgites (04LH34A of site A is an exception) have concomitant elevations of 187Re/188Os and 185Os/188Os above values of 0.1 and 0.120, respectively. Lherzolites and composite-lherzolites have 187Re/188Os compositions ranging from 0.32 ± 0.003 to 0.55 ± 0.006, and chondritic to supra-chondritic 185Os/188Os values (0.1246–0.1324). Sample 04LH07A, associated with hornblendite-veinlets,
has unusual Re–Os isotope compositions compared to other lherzolites analysed in this work; the bulk $^{187}\text{Re}/^{188}\text{Os}$ value of 0.36 ± 0.004 falls within the range of other lherzolite samples, but 04LH07A has the lowest $^{187}\text{Os}/^{188}\text{Os}$ composition (0.11258 ± 0.00010) of all studied specimens. The highest $^{187}\text{Re}/^{188}\text{Os}$ (0.73 ± 0.007) and $^{187}\text{Os}/^{188}\text{Os}$ (0.1387) isotope compositions yet reported for the Lherz massif (Fig. 7) were determined for olivine-websterite 04LH38.

Regional studies of Ariège-group peridotites identified broad linear correlations between $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$, and relatively strong positive correlations between $^{187}\text{Os}/^{188}\text{Os}$, S and Al$_2$O$_3$ contents (Reisberg and Lorand, 1995; Burnham et al., 1998) that overlap the range of Os–Al values reported here. New results for the Lherz massif alone show that bulk-rock $^{187}\text{Os}/^{188}\text{Os}$ values of the studied sample suite do not correlate linearly with $^{187}\text{Os}/^{188}\text{Os}$, S, Al$_2$O$_3$, MgO, Yb (e.g., Fig. 7 and Appendix B). Harzburgites generally cluster at low $^{187}\text{Os}/^{188}\text{Os}$, $^{187}\text{Re}/^{188}\text{Os}$, S, Al$_2$O$_3$, MgO, and Yb values, whereas lherzolites ± olivine-websterite form a cluster at higher S, Al$_2$O$_3$, MgO, and Yb contents with $^{187}\text{Os}/^{188}\text{Os}$ values overlapping the range of Os-isotope compositions reported for recently exhumed abyssal peridotites that sample present-day convecting upper mantle (e.g., Fig. 9b), and similar observations have been described for Middle-Atlas peridotite xenoliths (Wittig et al., 2010).

### 4. PETROGENETIC MODELS

The Lherz body lacks dunite and contains relatively small volumetric proportions of harzburgite, thus it differs from harzburgite dominated massifs associated with ophiolite sequences that generally contain cross-cutting dunite channels, which have been linked to melt generation at high melt-flux rates (e.g., Canyon Mountain, Oregon; Josephine, Oregon, Semail, Oman; Troodos, Cyprus, Red Mountain, New Zealand; Dick and Sinton, 1979; Boudier and Nicolas, 1985; Kelemen et al., 1995). The entire range of bulk-rock and spinel major-element compositions reported for Lherz differ from SSZ-peridotites that may have equilibrated with boninitic magmas (e.g., spinel Cr# > 60 reported for peridotites of the Izu–Bonin–Mariana Arc, Parkinson and Pearce, 1998) and their experimental equivalents (e.g., Gaetani and...
However, highly-depleted (whole-rock Al₂O₃ <0.85 wt.%) hornblendite-free harzburgites of site A, with bulk-rock trace-element contents analogous to mantle-wedge peridotites (e.g., Avacha peridotite xenoliths; Ionov, 2010), contain low-Ti clinopyroxenes that are similar to those reported for subduction-zone peridotites of the Hellenic ophiolite and Izu–Bonin–Mariana arc peridotite suites (Fig. 6c and d). Many of the studied peridotites from the Lherz body have bulk-rock and mineral major-, minor-, and trace-element compositions that are transitional between abyssal and SSZ-peridotites (e.g., Fig. 6; Appendices A and B), and for these reasons the following discussion examines whether the studied range of peridotite ± olivine-websterite compositions can be accounted for by: (1) percolative refertilisation of refractory peridotites with basaltic melt; (2) variable degrees of melt depletion followed or accompanied by physical mixing of peridotite and pyroxenite during mechanical mingling; (± short-length scale melt-interaction at pyroxenite margins); and (3) short-length scale metasomatism unrelated to postulated Ca, Al, Ti, Fe enrichment envisaged in models of igneous-refertilisation. We also evaluate the tectonic setting in which melting and olivine-websterite formation may have taken place.

4.1. Assessment of percolative igneous refertilisation

Models of igneous refertilisation constructed by two-component mixing between harzburgite 04LH33 and experimental melts (analogous to primary melts that could be envisaged in a zone-refining scenario) produce a broad field of products overlapping the range of lherzolite Mg–Fe–Si compositions at site B, and the majority of compositions observed in the banded-lherzolite body at site A (Fig. 3b). However, the orientation of the elongate fields of harzburgite at site A and B, and the field of site B lherzolite Mg–Fe–Si compositions cross-cut the trajectory of these igneous refertilisation models. In this context, the range of melt compositions required to satisfy the observed bulk-rock compositions does not follow a single refertilisation trajectory and requires interaction with substantial melt volumes (≥ 5-10 wt.% of the product) ranging from basanite to tholeiite. The requirement of significant melt volumes of distinct major-element compositions coexisting in closely spaced samples (10 s cm scales) during a percolative igneous refertilisation process is difficult to envisage as a physically realistic aspect of melt infiltration. Hand-specimen, mineralogical, and bulk compositional data show that site A lherzolites represent physical mixtures of lherzolite + olivine-websterite, and field observations indicate that this process is structurally old and took place under conditions where plastic-deformation operated. Site B lherzolites are heterogeneous and may also contain a websteritic component, but the interpretation of this group of samples is complicated by modal-metasomatism that formed secondary pyroxene ± spinel ± amphibole ± sulphide accompanied by cryptic-metasomatism that elevated LREE and MREE abundances of bulk-rocks and clinopyroxenes during the formation of late-stage cross-cutting hornblendite-veinlets.
4.2. Spinel-facies harzburgite formation

Bulk-rock MgO, Mg#, Al2O3, and HREE abundances of the studied peridotites correlate with one another and trace the extent of melt extraction in relatively homogenous samples unaffected by recent interaction with basanitic magmas associated with hornblende formation. For these reasons moderately-compatible and compatible-element compositions of harzburgites reflect the conditions of melt generation. The highest degrees of melting are recorded by harzburgites (up to ~25 wt.% melt loss; Appendix B), which have Mg–Fe–Si abundances and relatively high olivine/orthopyroxene values (olivine/orthopyroxene = 2.08–5.76) that cannot be accounted for by anhydrous melting alone (Fig. 3a and Fig. A3 of Appendix A). Low-Al harzburgites of site A contain clinopyroxenes with low-alkali contents; the low-Ti abundances of these clinopyroxenes differ from residual clinopyroxenes of abyssal peridotids (Fig. 6c and d), but are broadly analogous to clinopyroxenes of SSZ-peridotides. However, clinopyroxene and bulk-rock trace-element data for these rocks lack pronounced enrichment of Cs, Rb, Ba, and Pb, suggesting that these materials did not form in an environment that experienced high-rates of fluid flux from subducted lithosphere (i.e., not within ~100 km of a slab-wedge interface; Pearce and Parkinson, 1993; though this parameter is dependent on nature of subducting materials, the angle of dip of the subducting slab, and the maturity of the subduction-zone system). The lack of correlation between harzburgite incompatible-element abundances and orthopyroxene/olivine values (not shown) suggests that it is unlikely that orthopyroxene is of secondary origin, and significant degrees of interaction with Si-bearing melts/fluxes are doubtful. Mineralogical affinities between peridotite bands of the Lherz massif, abyssal (Fig. A3, Appendix A) and SSZ-peridotides (e.g., Fig. 6), which are thought to be derived from melting over an interval that does not exceed 2 GPa (c.f. Kinzler, 1992; Walter, 2003 and references therein), lead us to examine trace-element constraints on the depth at which melting took place to produce the peridotites of the Lherz massif.

The studied sample set displays a wide-range of trace-element characteristics, which indicates that Lherz peridotites have a complex metamorphic history (appraised in Section 4.3). We focus on constraining the genesis of site A harzburgites as the origin of site B harzburgites is obscured by Al, Fe, Ti, Na, LREE, and MREE enrichment resulting from interaction with hornblende forming magmas. Moderately-incompatible element contents of peridotites may be significantly less susceptible to post-melting modification than incompatible elements, and for this reason HREEs are used to constrain melting style. Previous authors have used bulk-rock Tm–Yb compositions to suggest that the Lherz peridotites result from variable degrees of garnet-facies melting (i.e., in excess of 2 GPa; Bodinier et al., 1988; Burnham et al., 1998). New trace-element data for the Lherz peridotites, combined with that of previous studies, show that harzburgites generally have a positive slope between HREEs, and bulk-rock Dy–Yb and Lu–Hf contents (Fig. 6 and Fig. A7 of Appendix A) define arrays analogous to residue compositions expected for spinel-facies melting. Hornblende-free harzburgites and constituent clinopyroxenes generally have positive MREE–HREE slopes, and this contrasts to negative MREE–HREE slopes of clinopyroxenes of abyssal peridotites exhumed at slow-spreading ridges where the earliest stages of melting take place in the presence of garnet followed by significant degrees of fractional melting in spinel-facies mantle (e.g., Johnson et al., 1990; Johnson and Dick, 1992; Hellebrand et al., 2002, 2005). For these reasons Lherz harzburgites may have experienced melting under slightly shallower conditions (or over a narrower melting interval) than many of the abyssal peridotites studied to date.

Models were constructed for fractional melting of a primitive-mantle (McDonough and Sun, 1995) source, and the precise composition of predicted residues is sensitive to the selected partition coefficients, melting modes, and starting composition. The range of Dy–Yb compositions in Lherz peridotites defines a fractionation curve sub-parallel to melting curves calculated for residue compositions expected for fractional melting of fertile peridotite (analogous to primitive mantle (McDonough and Sun, 1995), fertile-MORB mantle (FMM; Pearce and Parkinson, 1993), or DMM (Workman and Hart, 2006)) in the spinel-facies (Fig. 6a). Compared to residue compositions expected for spinel-facies melting under anhydrous conditions, Lherz harzburgites have consistently lower Yb-abundances over a range of Dy/Yb values. Experimental studies have suggested that HREEs may be less compatible during fluid-present melting (e.g., Gaetani et al., 2003; McDade et al., 2003, and for this reason the relatively low HREE-contents of Lherz harzburgites indicate that they are residual after fluid-present melting (Fig. 6a). Abundances of V–Yb–Sc in these harzburgites are broadly consistent with models of melt depletion under oxidation conditions of FMQ to FMQ+1 (Fig. 6b and Fig. A7 of Appendix A), but the highest V-abundances determined for site A harzburgites, while overlapping the range reported for subduction-zone peridotites of Avacha and Izu–Bonin–Mariana, correspond to samples displaying the greatest degree of LREE-enrichment that may be linked to secondary processes. Earlier studies of oxidation conditions, which used olivine–orthopyroxene-spinel major-element equilibria (Woodland, 1992; Woodland et al., 1996, 2006), suggested that spinel-peridotites of the Lherz massif have oxidation states ranging from QFM – 1.5 to QFM + 1; which are transitional between fO2 values reported for abyssal peridotites and continental xenolith suites. Differences between fO2 conditions indicated by V-abundances determined in this study compared to previous studies of olivine–orthopyroxene–spinel equilibria (e.g., Woodland, 1992; Woodland et al., 1996, 2006) may reflect partial or complete resetting of oxidation records after melt extraction, and resolving the cause of these differences is beyond the scope of this work. Importantly, results of modelling the behaviour of moderately compatible trace-element compositions (Dy, Yb, Lu, Hf, V, and Sc) during melting are consistent with bulk-rock major-element and mineralogical characteristics that suggest harzburgites result from ~20–25 wt.% melt removal (Appendix B) in the absence of residual garnet (Fig. 6a and b, Fig. A7b and c of Appendix A), and a starting composition broadly analogous to FMM and/or DMM is in agreement with previous results for melt-
4.3. Modification of Lherz peridotites by melt- and fluid-metasomatism

Incompatible- and highly-incompatible element contents (including LREE, Zr, and Sr) of bulk-rocks and pyroxenes cannot be accounted for by models of melt extraction, and may have been modified after an earlier melting event. Previous authors have suggested that the range of trace-element abundances reported for Lherz peridotites may be explained by hydrous, carbonatite, and silicate-melt metasomatism that may reflect two distinct processes; (1) multi-stage metasomatic interaction with several generations of compositionally distinct melts/fluids (e.g., Woodland et al., 1996; Burnham et al., 1998; Fabriés et al., 1998, 2001); or (2) pervasive melt-infiltration accompanied by a chromatographic melt-front (e.g., Bodinier et al., 1988; Bodinier et al., 1990; Le Roux et al., 2007, 2008, 2009).

New trace-element data for harzburgite–lherzolite outcrops with contrasting pyroxenite and structural characteristics are consistent with the occurrence of two distinct metasomatic events. The first metasomatic event is characterised by cryptic metasomatism of harzburgites at site A and B; these samples display LREE-enrichment relative to HREE and MREE, have relatively high chondrite-normalised U and Th contents compared to Ba and Nb (pronounced in site A harzburgites). These samples lack pronounced enrichment of Cs, Ba, and Pb, that is generally associated with SSZ-melts that impart a distinctive trace-element signature linked to fluid release close to the slab-wedge interface (e.g., Pearce and Parkinson, 1993; Parkinson and Pearce, 1998). The lack of Ti-enrichment (Figs. 5 and 6c and d), absence ofapatite, and the lack of a linear correlation between clinopyroxene abundances, orthopyroxene/olivine values, and LREE-abundances and LREE/HREE values (of bulk-rocks and constituent pyroxenes; not shown refer to Appendix B), combined with the range of bulk-rock and pyroxene Zr abundances (Appendix B) suggest that LREE-enrichment in hornblende-free harzburgites is the result of post-melting interaction with: (1) a low-volume Si-poor fluid phase, (2) a low-volume volatile-bearing melt, or (3) a combination of these (c.f., Rudnick et al., 1993; Schiano and Clōchichiatti, 1994; Schiano et al., 1995; Xu et al., 2003; Bouvier et al., 2010a,b for relevant comparisons). No fluid inclusion data are currently available for the Lherz massif, but at least two generations of CO₂-H₂O bearing fluids thought to have equilibrated at temperatures of ~950 °C and pressures of 6–7 kbar and 8–9 kbar, respectively, have been reported in this region for amphibole-bearing peridotites of the Cassou massif (Fabriés et al., 1989; Bilal, 1978), and fluids of broadly similar compositions may be responsible for a significant portion of LREE, and Sr, enrichment in hornblende-free harzburgites.

The second metasomatic event identified in this study postdates earlier LREE-enrichment linked to Si-poor fluids/melts, and involves modal (amphibole ± phlogopite ± sulphide ± secondary pyroxene) and cryptic metasomatism (MREE-enrichment, intermediate Cr/Al values, and relatively high bulk-rock and pyroxene Ti and Na contents in the absence of secondary minerals) linked to the formation of hornblende-veinlets at site B. These mineralogical and chemical enrichment characteristics are consistent with results reported in earlier studies of melt–rock interaction adjacent to amphibole-bearing veins (e.g., Bodinier et al., 1987b; McPherson et al., 1996; Woodland et al., 1996; Bodinier et al., 2004). Outcrop relationships suggest that hornblende-vein formation is a relatively recent event, and previous studies indicated that hornblendites crystallised at ~100 Ma (e.g., Henry et al., 1998) at relatively low-pressures (e.g., <1.3 GPA; Fabriés et al., 2001; Lorand and Gregoire, 2010). Conquéred and Fabriés (1984) indicated that hornblendites intrude along compositional boundaries between harzburgite and lherzolite, and our own observations suggest that this may be the case at site B. In addition, new spatial information related to LREE-enrichment at site A suggests that the lithological boundary between adjacent harzburgite and lherzolite bodies represents a conduit that facilitated post-melting fluid ingress, and both site A and B demonstrate that pre-existing structural features can focus fluid and/or melt flow in mantle materials.

4.4. Petrogenesis of Ol-websterite bands and associated Lherzolites

The majority of the studied lherzolites are composite samples with distinct textures at the two study sites. Samples of the banded-lherzolite body of site A contain websterites that are generally thick (up to 8 cm wide), foliation parallel, and laterally extensive (10 s of metres). Websterite bands of site A plot on an extension of bulk-rock major-element covariation trends defined by Lherz peridotites (e.g., Fig. 2a). Major-element compositions (e.g., Mg#) of site A olivine-websterites do not solely reflect equilibrium and fractional crystallisation of a basaltic melt (c.f. crystallisation experiments of Villiger et al., 2004, and references therein for a discussion of experimental constraints on basalt crystallisation processes), and differ from crystallisation products derived from H₂O-undersaturated melts (up to 5 wt.% H₂O) at 1.2 GPA (e.g., Müntener et al., 2001). Although modal abundances and mineralogical compositions of olivine-websterites cannot be accounted for by products of crystallisation experiments performed to date, published experimental work has generally used starting materials with Mg# ≤ 70 (c.f. Müntener et al., 2001; Villiger et al., 2004, 2007 and references therein). Major-element compositions of olivine-websterites tend toward the composition of clinopyroxene (e.g., Fig. 3c), do not lay on a tie-line between clinopyroxene and orthopyroxene, and while they probably represent cumulate bands in the broadest sense (c.f. Dantès et al., 2007 and a review by Downes, 2007), it is unclear if pyroxene-segregation during channelled magma flow (e.g., Irving, 1980) significantly influenced their compositions.

Equilibrium melts calculated from trace-element compositions of clinopyroxenes indicate that lherzolites and olivine-websterites are in equilibrium with a LREE-enriched melt (Appendix B). The absolute concentrations of REE in the calculated melt are dependent upon the choice of partition coefficients (and the conditions for which they are relevant), but all calculated melts are consistently LREE-enriched. This melt composition is distinct from that of bulk-rock olivine-websterites, and REE contents of equilibrium melts are broadly analogous to E-MORB (Sun and McDonough, 1989), and continental tholeiites parental to Triassic Pyreanean dolerites (e.g., Albert, 1985) when anhydrous partition coefficients are applied. Downes (2001) used lithophile-element isotope compositions to show that no direct link between the lherzolites of Lherz and Pyreanean dolerites exists (e.g., Downes, 2001).

LREE-enriched basalts and parental melts have been identified in back-arc basin environments (e.g., Pearcy et al., 1990; Stern et al., 1990), and for this reason REE compositions do not provide unique information to constrain the environment in which lherzolites and olivine-websterites formed. The presence of amphibole in the studied specimens, and major and trace-element evidence of fractionation controlled by olivine + clinopyroxene in the absence of garnet (e.g., Figs. 3c and 6a) may suggest that partition coefficients determined for mantle-wedge environments are more appropriate. The application of partition coefficients reported for mantle-wedge conditions (e.g., Pearce and Parkinson, 1993; Gaetani et al., 2003; McDade et al., 2003) indicates that melts in equilibrium with lherzolite and olivine-websterite pyroxenes have Cr and Y abundances that overlap the compositional range reported for island-arc tholeiites (IAT), back-arc basin basalts (BABB), and MORB produced by melting of a relatively fertile mantle source (c.f. Fig. 8 of Pearce et al., 1984, Appendix B). Titanium–vanadium ratios of these equilibrium melts are <20, and this is consistent with Ti/V values expected for back-arc basin settings (c.f. Sheriffs, 1982 for a discussion of Ti/V variation in basalts of distinct provenance). Nio- bium contents calculated for these equilibrium melts (generally 1–4 ppm) are broadly analogous to those of N-MORB, and are lower than Nb concentrations typical of EMORB and OIB (2.33 ppm, 8.30 ppm and 48 ppm, respectively; Sun and McDonough, 1989). The similarity of equilibrium liquid compositions among olivine-websterites and adjacent lherzolites suggests that these rocks are genetically related. The simplest explanation of the current major- and trace-element data set in closely-spaced lherzolites and olivine-websterites is that olivine-websterites represent pyroxene-rich cumulates of a tholeiitic LREE-enriched melt that crystallised in melt-flow channels created during moderate degrees of melting (<15 wt.% melt removal; Bodinier et al., 1988; Burnham et al., 1998), and this differentiation event may also have formed residual lherzolites. In this sense site A banded-lherzolites may be broadly analogous to thin-layer peridotites and pyroxenites of the Horoman massif where pyroxene forming melts are not thought to cause significant refertilisation (i.e., Al, Ca, Ti addition) of adjacent peridotites (Malaviarachchi et al., 2010).

4.5. Re–Os: timing of lithosphere stabilisation or inherited upper-mantle heterogeneity?

Samples of the Lherz massif are characterised by Re and Os abundance variations with bulk-MgO content that indicate Re and Os behave as moderately-incompatible and compatible elements, respectively, and this observation is broadly consistent with previous studies of Re–Os behaviour in basaltic silicate melt systems (e.g., Pearson et al., 2004). Rhenium-Os isotope compositions of Lherz peridotites ± olivine-websterite do not define a statistically meaningful isochron (e.g. Fig. 7a and b; large MSWD ∼ 1), nor do they coincide with mixing curves that approximate igneous refertilisation (constant addition of basaltic melt to refractory peridotite) recently, at 100–500 Ma (corresponding to the time of hornblende formation, and including the period of late-Variscan thermal events), and at 0.5 Ga intervals between 1 Ga and 3.5 Ga (Fig. 8). The large difference between the relatively low Os contents of basalts (typically 10–500 ppt) compared to the high Os abundances in mantle materials (generally on the order of 3000–5000 ppt), where the majority of the osmium is hosted by Os-rich sulphides ± Os–Ir-alloys associated with olivine (e.g., Luguët et al., 2007), mean that 187Os/188Os compositions of peridotites will not be significantly disturbed by small to modest degrees of melt–rock interaction, particularly when interaction has taken place within the last 1 Ga (Fig. 8). For these reasons, osmium isotope compositions of individual bulk-rock peridotites, while strictly reflecting the sum of a mixed phase population (e.g., Lorand, 1991; Burton et al., 1999; Alard et al., 2000; Harvey et al., 2006, 2010, 2011; van Acken et al., 2008, 2010; Lorand et al., 2010; Lorand and Alard, 2011), probably record the approximate time of melt-depletion as volumetrically minor Os-rich trace-phases may account for >90% of the bulk-rock Os content (c.f. Harvey et al., 2010 for a study of the effects of variable degrees of melt/fluid metasomatism on Os-isotope compositions).

The lack of an isochronous bulk-rock Re–Os isotope relationship reflects the fact that the Lherz body comprises intercalated units of distinct lithologies where harzburgites may not be strictly coeval with lherzolite ± olivine-webste-rite, and these materials may have evolved with variable initial 187Os/188Os compositions from ~1.6 Ga onwards. Additionally, a comparison of Re–Os isotope data to a 1.6 Ga reference line (Fig. 7) indicates that some samples have higher Al2O3 and Re abundances at a given 187Os/188Os composition, and this probably reflects recent Re and Al disturbance that may be linked to hornblende-rite-interaction that has not significantly disturbed 187Os/188Os values. The 187Os/188Os isotope compositions of harzburgites generally yield TRD ages (representing a minimum differentiation age: Shirey and Walker, 1998) of ~1.4 to 1.5 Ga (Fig. 9b). The period of isolation required to generate the observed 187Os/188Os values in composite-lherzolites and olivine-websterites with suprachondritic Re/Os values is in broad agreement with TRD ages of harzburgites, assuming that these materials have experienced a single-stage evolution with respect to Os.

Osmium isotope compositions do not offer highly-pre- cise geochronological information (c.f. review by Rudnick
and Walker, 2009), but do provide broad constraints on the timing of ancient differentiation. Meso-Proterozoic Os-ages determined here are; (1) similar to model ages derived from the Os–Al correlations generated from our study focused on constraining the petrogenesis of the oldest portions of the Lherz massif (foliation parallel lithological strips); (2) within error of Os-model ages reported for peridotites that include ultramafic samples from an ESE–WNW traverse of >300 km of the Pyrenean chain (Reisberg and Lorand, 1995; Burnham et al., 1998); and (3) overlap Nd-model ages reported for the oldest portions of western European crust where structurally divided I- and S-type granites have been linked to ancient subduction systems (e.g., ~1.7 to 1.4 Ga; Liew and Hofmann, 1988). Crustal materials of central and western Europe for which Liew and Hofmann (1988) reported Meso-Proterozoic Nd-model ages do not have a direct genetic link to ultramafic bodies of the Pyrenees, but these authors suggested that crustal materials of the Maldonian zone (including central and southern France) may be linked to a Proterozoic continental mass to the south, and this crustal mass could potentially be related to the genesis of Ariège-group massifs (c.f. Burnham et al., 1998). Further studies are required to constrain the composition, origin, and evolution of the oldest crustal materials within the Pyrenean chain, and this information, combined with further knowledge of peridotite emplacement mechanisms, may then be used to provide a more rigorous assessment of crust–mantle relationships in this region.

Osmium-Al values reported for the Lherz peridotite body overlap and extend to higher and lower $^{187}$Os/$^{188}$Os values than those reported for other Ariège-group ultramafic massifs that define a broad positive correlation with bulk-rock $\text{Al}_2\text{O}_3$ (Fig. 9a), and such trends, when broadly supported by correlations between $^{187}$Os/$^{188}$Os compositions and Re/Os abundance and isotopic ratios (Appendices A and B), are generally considered to reflect long-term isolation from the homogenising environment of the convecting upper mantle (e.g., Reisberg and Lorand, 1995; Burnham et al., 1998). However, the recent discovery of a broad Os–Al correlation in modern convecting upper mantle (Fig. 9a, spinel-facies peridotites exhumed at the ultra-slow-spreading Gakkel Ridge (1.4–0.7 cm/year; Michael et al., 2003) that yields an ancient model-age (~2 Ga; Liu et al., 2008) increases uncertainty about the geological meaning of Os-ages determined for ultramafic materials of Proterozoic and Phanerozoic terranes. The range of $^{187}$Os/$^{188}$Os isotope compositions reported for samples from the Lherz massif overlaps the spread of abyssal peridotite Os-isotope compositions, but Os–Al correlations and $^{187}$Os/$^{188}$Os frequency distributions of Lherz samples differ from abyssal peridotites in detail (Fig. 9b). Mid-Atlantic Ridge (Brandon et al., 2000; Harvey et al., 2006) and Izu–Bonin–Mariana peridotites (Parkinson et al., 1998) form discrete data clusters covering a range of $^{187}$Os/$^{188}$Os compositions with limited variation in bulk-rock $\text{Al}_2\text{O}_3$ abundances, and this is distinct from the distribution of Os-isotope and $\text{Al}_2\text{O}_3$ compositions for samples of the Lherz massif. When compared to all available $^{187}$Os/$^{188}$Os data for abyssal peridotites (Fig. 9b) a greater proportion of $^{187}$Os/$^{188}$Os compositions reported for the Lherz massif are subchondritic, clustering at $T_{\text{Re}}$ ages of ~2 to 1.5 Ga. The broad correlation between $^{187}$Os/$^{188}$Os isotope compositions and bulk-rock $\text{Al}_2\text{O}_3$ abundances that encompasses Lherz and many other Pyrenean ultramafic massifs (sampling an area >300 km in length) exhumed in a mountain belt with a significant collisional history (c.f. McCann, 2008a,b; Garcia-Sansegundo et al., 2011), lead us toward a preferred model in which the oldest portions of the Lherz massif were created during Meso-Proterozoic melting linked to the formation of overlying crust. New mineralogical and trace-element data for Lherz peridotites ± olivine-websterite indicate that the oldest portions of this massif represent materials from mantle-wedge environments, and fluid-present spinel-facies melting may have taken place in a back-arc basin setting. For these reasons subduction zone processes may have been active at the boundary between the Iberian and European plates during the Meso-Proterozoic, and this may be a regionally important aspect of crustal growth.

An important outcome of this study is new compositional information that suggests a link between high degrees of melting in shallow, subduction-influenced environments that may be responsible for the formation Pt–Ir–Os alloys identified in harzburgites produced by 20–25 wt.% melt removal (e.g., those studied by Luguet et al., 2007). Pt–Ir–Os alloys ± laurite-erlichmanite sulphides may form as the point of S-exhaustion is approached during mantle melting (c.f. Luguet et al., 2007). Complete removal of S during low-pressure, subduction influenced melt generation is consistent with experimental evidence that indicates such environments probably produce primary melts with high S contents at sulphur saturation (>1300 ppm) capable of relatively high-degrees of S-removal from the residue when compared to melting at pressures >2 GPa (e.g., Mavrogenes and O’Neill, 1999; Holzheid and Grove, 2002; Jugo, 2009). Isolated minerals with high Os contents created during melting to the point of S-exhaustion are essentially devoid of Re, have relatively high-melting temperatures (>1300 °C; e.g., Andrews and Brenan, 2002), and may preserve records of ancient mantle differentiation in materials that have a multi-stage history of magmatism and solid-state mixing (Luguet et al., 2007). Thus, the geochemical properties of Os mean that bulk-rock, Pt–Ir–Os alloy, and primary laurite-erlichmanite Os-isotope compositions provide a powerful record of ancient, large-volume differentiation events, and statistical assessment of such information (e.g., Pearson et al., 2007), in the context of well-defined petrological constraints, is of great importance for determining: (1) the timing and mechanisms of local, regional, and global crust–mantle evolution; and (2) the proportion of refractory material present in Earth’s heterogeneous upper mantle.

5. SUMMARY AND IMPLICATIONS

New compositional data for closely spaced samples recovered from two traverses of adjacent harzburgite and lherzolite bodies ± olivine-websterite show that percolative igneous refertilisation during the Variscan is not a viable
process to explain the range of major- and trace-element abundances, and Re–Os isotopic compositions reported for the Lherz massif. Field, textural, and compositional data indicate that the Lherz massif is composed of elongate, foliation parallel, lithological strips that were juxtaposed during plastic deformation. Major-element oxide, bulk-rock and clinopyroxene trace-element compositions show that highly-depleted harzburgites result from ~20–25 wt.% melt extraction, are analogous to some mantle-wedge peridotites (e.g., Avacha xenoliths), and were created at pressures < 2 GPa. In contrast, the studied lherzolites ± olivine-websterite are heterogeneous and represent physical mixtures of residual materials and clinopyroxene-dominated cumulates equilibrated with a LREE-enriched tholeitic melt that formed in the absence of residual garnet. Two metasomatic events have modified peridotite compositions; the first involves wide-spread percolation of a Si-poor melt/fluid; and the second is evident at site B where relatively recent, small-volume melt interaction is linked with the intrusion of hornblende-veinlets at the compositional boundary between adjacent harzburgite and lherzolite bodies. In addition, new mineral major-element data indicate that the intercalated peridotite + pyroxenite assemblages of the Lherz ultramafic body equilibrated at lithospheric conditions (temperatures of ~800–900 °C or less), and previous studies of lithophile-element isotope compositions suggested that cooling and recrystallisation occurred during the Cretaceous (Henry et al., 1998 and references therein).

Rhenium-Os systematics in this suite of samples show that Os behaves compatibly and 187Os/188Os compositions have not been significantly disturbed by small-volume melt interaction. Osmium-isotope compositions, combined with literature data for other Ariège-group ultramafic bodies, define a broad positive correlation with bulk-rock Al2O3 abundances indicating that harzburgites, lherzolites, and olivine-websterites have been isolated from convective homogenisation since the Meso-Proterozoic and this broadly coincides with the time at which melting created the residual materials. The association between harzburgites resulting from spinel-facies melting in mantle-wedge environments and residual, Os-rich, laurite-erlichmanite sulphides and Pt–Os–Ir-alloys suggests that a substantial proportion of persistent refractory anomalies in the present-day convecting mantle of Earth may be linked to ancient large-scale melting events that may in turn be related to subduction processing.

ACKNOWLEDGMENTS

Dr. B.L.A. Charlier is thanked for his guidance during the doctoral study of A.J.V. Riches. In addition, we are grateful to Dr. A. Gannoun for support during Re–Os isotope analyses, Dr. S. Hammon for guidance during measurement of trace-element concentrations, Dr. John Watson for his assistance during XRF analyses, and we are indebted to Michelle Higgins and Kay Green for the preparation of many fine polished sections. Dr. H. Downes and Dr. I.J. Parkinson are thanked for their encouragement and remarks on a previous version of this work, and Dr. M. Bizimis, two anonymous reviewers, and the Associate Editor, Dr. S. Huang, are thanked for their astute comments on an earlier draft of this manuscript. This work was supported by a NERC studentship (Grant Number NER/S/A/2004/13014) to A.J.V. Riches.

APPENDIX A. SUPPLEMENTARY DATA


REFERENCES


Alibert C. (1985) A Sr–Nd isotope and REE study of late-Triassic dolerites from the Pyrenees (France) and the Messejana Dyke (Spain and Portugal). Earth Planet. Sci. Lett. 73(1), 81–90.


Villinger S., Ulmer P. and Müntener O. (2007) Equilibrium and fractional crystallisation experiments at 0.7 GPa; the effect of pressure on phase relations and liquid compositions of tholeiitic magmas. J. Petrol. 48(1), 159–184.


