Dating layered websterite formation in the lithospheric mantle

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Abstract

Pyroxenites are often documented among exhumed mantle rocks, and can be found in most tectonic environments, from supra-subduction to sub-continental and sub-oceanic mantle. In particular, websterites, i.e. orthopyroxene-clinopyroxene bearing pyroxenites, are found in parallel layers in most orogenic and ophiolitic peridotites. Their formation is often ascribed to melt infiltration and melt-rock reaction processes accompanied by variable amount of deformation. One outstanding question is whether the ubiquitous occurrence of layered websterites in exhumed rocks is generally linked to the exhumation process or truly represents large-scale melt infiltration processes at depth prior to exhumation. These two hypotheses can be distinguished by comparing the exhumation and formation ages of the websterites. However, determination of the layered websterite formation age is challenging. Here we present a novel approach to constrain the formation age of websterite layers using samples from the Lherz massif (France), where layered websterites and lherzolites have formed through melt-rock reaction. By combining high-resolution REE variations, isotope model ages, and diffusive re-equilibration timescales using REE closure temperatures across the websterite layers, we constrain a minimum

age and a maximum age for the formation of layered websterites. We show that layered websterites in Lherz formed 1,500-1,800 Ma ago, and are thus clearly disconnected from the process of exhumation at 104 Ma. Multiple generations of layered websterites commonly found in ultramafic massifs, along with the evidence for ancient melt-rock reaction in Lherz, indicate that melt-rock reactions can happen episodically or continuously in the mantle and that layered websterites found in exhumed mantle rocks record ubiquitous melt infiltration processes in the mantle.

1. Introduction

Pyroxenites are commonly found in exhumed mantle rocks from supra-subduction, sub-continental and sub-oceanic environments. They display a large chemical and mineralogical variability, from garnet pyroxenite to websterite, clinopyroxenite or orthopyroxenite, and may occur in dykes, single veins or layers. Chemical and mineralogical features of pyroxenites indicate that their diversity originates from a combination of processes (e.g., France et al., 2015; Lambart et al., 2013), ranging from crystal fractionation from melts generated by melting of a recycled oceanic crust (e.g., Pearson and Nowell, 2004), to re-melting of older layers and melt-rock reactions (e.g., Garrido and Bodinier, 1999). This study specifically focuses on the formation of parallel layers of websterite (Fig. 1), which are found in many orogenic and ophiolitic peridotites. There, they can represent a few percent by volume of exhumed lithosphere and can be locally predominant over peridotites.

In Ronda (Spain), Beni Bousera (Morocco), and Lherz (France), combined structural and geochemical studies have shown that layered websterites are most likely the result of melt-rock

reactions (Bodinier et al., 2008; Garrido and Bodinier, 1999; Gysi et al., 2011; Le Roux et al., 2007; Soustelle et al., 2009). Melt infiltration and melt-rock reaction processes, along with variable melt-rock ratios, have also been suggested to explain websterite layers at the base of the Kohistan arc (Burg et al., 1998), in the Totalp ultramafic massif (van Acken et al., 2010), in the Josephine peridotite (Le Roux et al., 2014), and in the Balmuccia massif (Rivalenti et al., 1995), among others. In this scenario, asthenospheric melts solidify within the peridotite matrix (e.g. Bodinier et al., 2008; Garrido and Bodinier, 1999; Le Roux et al., 2007; Lenoir et al., 2001; Soustelle et al., 2009), and websterites form by melt consuming reactions where pyroxenes crystallize at the expense of olivine.

However, it is uncertain whether melt-rock reactions that formed layered websterites are related to local exhumation, or whether they are ubiquitous processes at depth, unrelated to exhumation. For example, several generations of pyroxenites have been identified in the Ronda and Beni Bousera massifs, and some of them, although not dated, have been tentatively ascribed to exhumation (e.g., websterites in the plagioclase-tectonite domain of Ronda; Bodinier et al., 2008). Comparing the age of exhumation and the age of layered websterites can shed light on this question, while the challenge lies in determining the exact ages of formation. To our knowledge, a limited number of studies have estimated the age of formation of layered websterites and investigated the relationship between the age of melt-rock reaction and the exhumation age of layered websterites. For example, Sm-Nd isochrons defined by pyroxenites and wall-rock peridotites in the External Ligurides (Italy) indicate that pyroxenites formed ~ 300 Ma before exhumation of the massif at 160 Ma (Borghini et al., 2013). Similarly, Re-Os model ages in garnet-bearing websterites from the Beni Bousera massif ('type III' pyroxenites in Gysi et al. 2011) suggest that the age of exhumation of the massif (< 26 Ma) and the model age of

formation of websterites and garnet pyroxenites (0.67-4 Ga) are disconnected (Pearson and Nowell, 2004). However, large uncertainties can be associated with radiogenic model ages, as they, in addition to closed system behavior since the time of crystallization, also rely on the assumption that the mantle evolved along a single evolution curve instead of occupying a field, as the present MORB mantle does. Other websterites in Beni Bousera have been ascribed to a later stage of melt infiltration and metasomatism, based on limited subsolidus reequilibration and undeformed textures ('type I' of Gysi et al. 2011). Those websterites resemble the 'group D' websterites of Ronda (Spain), but unlike them, did not replace older generations of layers (Garrido and Bodinier, 1999). Similarly, 'type II' websterites in Beni Bousera and 'group C' websterites in Ronda are also thought to have formed through melt-rock reactions (Garrido and Bodinier, 1999; Gysi et al., 2011), but no absolute age constraints have been determined.

Here we apply a novel combination of isotope model ages and diffusion modeling, which are two independent methods, to constrain the age of formation of layered websterites in the Lherz Massif (France) and compare it to its age of exhumation. On the one hand, we use the trace element composition of clinopyroxene in nine samples and the isotope signature of clinopyroxene in one sample (06LI17) from heavily percolated areas of the massif ('distal' samples) dominated by lherzolites and layered websterites to calculate the maximum model age at which the percolating melt reacted with the lithospheric mantle. On the other hand, we calculate the major and trace element closure temperatures in pyroxenes on seven thick sections from a 34-cm cross-section through harzburgites, lherzolites and layered websterites (composite sample LN12-18), at 200 m. or less from the 'distal' samples, and use diffusion modeling to calculate the time scale of trace element re-equilibration throughout the lithological transition, which produces a minimum age for the melt-rock reaction. Using these maximum and minimum

ages, we constrain a robust age range for the formation of layered websterites in the Lherz massif and discuss implications for the ubiquitous formation of layered websterites in the lithospheric mantle.

2. Geological context and samples

The Lherz massif is the type-locality of lherzolite and a distinct example of melt-rock reactions in the Earth's mantle (Le Roux et al., 2009; Le Roux et al., 2007; Le Roux et al., 2008). There, lherzolites and parallel Cr-diopside spinel websterite layers formed at the same time through melt-rock reaction (Le Roux et al., 2008) between a > 2 Ga year old (Reisberg and Lorand, 1995) harzburgitic lithosphere and asthenospheric basaltic melt. The process of melt-rock reaction, where olivine and melt reacted to form pyroxene and spinel, has been thoroughly documented throughout the whole massif with field relations (Le Roux et al., 2007), crystal-preferred orientations (Le Roux et al., 2008), isotope and trace element variations (Le Roux et al., 2009; Le Roux et al., 2007), and by in-situ sulfide chemistry (Lorand et al., 2010). The melt-rock reaction and deformation event recorded in lherzolites and websterites were most likely contemporary (Le Roux et al., 2008). The upper part of the Lherz massif is dominated by preserved pieces of unreacted harzburgitic lithosphere. There, sharp discontinuities exist between websterite layers, which alternate at cm-scale with reacted lherzolite and in some places, with depleted harzburgite (Fig. 1). The lower part of the massif has extensively reacted with the percolating melt and contain abundant, newly-formed, lherzolites and layered websterites, and only a few harzburgitic relics (see Fig. 1 in Le Roux et al., 2007). The lherzolites and websterites found in heavily percolated areas of the massif that outcrop > 10m or more away from any

contact with relic harzburgite are referred to here as ‘distal’ lherzolites-websterites or ‘distal’ samples. Those rocks have homogenous REE patterns (Le Roux et al. 2009), contain abundant websterite layers, and thus have been overprinted by the largest volumes of melt and approached equilibrium with the percolating melt.

Websterite layers experienced the highest extent of melt-rock reaction, which resulted in dissolving almost all olivines out of the harzburgitic protolith. In Lherz, the websterites contain 40-60 % orthopyroxene, 40-60 % clinopyroxene, and a few percent of olivine and spinel. Based on their Mg-number ($100 \times \text{Mg}/(\text{Mg} + \text{Fe})$ molar), Cr-number ($100 \times \text{Cr}/(\text{Cr} + \text{Al})$ molar) and Ti-number ($200 \times \text{T}/(2 \times \text{Ti} + \text{Al})$ molar) (Table S1), websterite layers from Lherz fall within ‘group C’ and ‘group D’ pyroxenites in Ronda (Garrido and Bodinier, 1999). While their major elements are more similar to ‘group D’ of Ronda (or ‘type I’ in Beni Bousera), their REE signature is more depleted like ‘group C’ of Ronda, or ‘type II’ of Beni Bousera. In those massifs, the diversity of layers has been generally attributed to metasomatism and melt infiltration processes. For example, ‘group C’ pyroxenites in Ronda were formed by melt-peridotite reactions at high melt-rock ratio, while ‘group D’ pyroxenites formed later, by reaction between peridotite and melt, and magmatic replacement of ‘group C’ layers (Garrido and Bodinier, 1999). In Beni Bousera, ‘type I’ pyroxenites record a melt infiltration stage that also produced refertilized lherzolites (like in Lherz) while ‘type II’ pyroxenites were attributed to reaction between a more evolved melt and peridotite (Gysi et al., 2011).

Exhumation of the massif into the crust has been dated at 104 ± 5 Ma (Henry et al., 1998). Because the exhumation age is already well constrained and the extent of melt-rock reactions that occurred in the massif has been thoroughly mapped, Lherz provides an ideal setting to determine the timing of formation of layered websterites formed by melt-rock reaction.

For the isotope model age calculations, ‘distal’ lherzolite-websterite samples collected in the lower part of the Lherz massif were used to determine the composition of the percolating melt and calculate isotope model ages. Among those ‘distal’ samples, the isotope signature and rare-earth element pattern of clinopyroxene in one sample have already been published (06LI17; Le Roux et al., 2009), and here we present the trace element patterns of clinopyroxenes in eight additional ‘distal’ samples. For the thermometry and diffusion modeling, the samples consist of parallel layers of harzburgite, lherzolite and websterite (Fig. 1) which were collected for this study in the upper part of the massif, but at 200 m. or less only from ‘distal’ lherzolite-websterite samples. Seven contiguous thick sections covered a 34-cm long section (LN12-18) roughly perpendicular to the harzburgite to lherzolite transition, which includes five cm-thick websterite layers and minor mm-thick websterite layers. New major and trace element analyses were performed across the lithological transitions in order to obtain a high-resolution (mm) image of chemical variations across the transition.

3. Methods

3.1. Electron probe micro-analyses

Major elements of harzburgites, lherzolites and pyroxenites were analyzed using a JEOL JXA-8200 electron microprobe at MIT. A 10 nA beam current and 15 kV accelerating potential were used for all analyses. Beam diameter was 1 micron. Data reduction was done using CITZAF software. The counting time used for the phase analyses was 40 s on peak, and 20 s on background. In order to prevent alkali diffusion, Na was analyzed for 20 s on peak and 10 s on

background. Major element compositions of clinopyroxene and orthopyroxene and reported in Table S1 and S2, respectively.

3.2. Laser ablation trace element analyses

Concentrations of trace elements in clinopyroxene and orthopyroxene from the 34-cm harzburgite-lherzolite-websterite layered cross section LN12-18 were analyzed in seven 150 μm thick sections using a single-collector inductively coupled plasma sector field mass spectrometer (Thermo Finnigan Element 2 ICP-MS) at Rice University (Table S2). A New Wave 213 nm laser ablation system was used for vaporization and an Ar-He gas mix was used for sample introduction. The laser was operated with a fluence of 20 J/cm², a pulse frequency of 10 Hz, and a spot size of 110 μm and signal integration time was 0.01 seconds. The elements Co, Ni, Cu, Zn, Y and Zr were analyzed in medium ($m/\Delta m \sim 3000$) resolution mode, while the elements Sr, La, Ce, Gd, Yb, Lu, Hf, Pb, Th and U were measured in low ($m/\Delta m \sim 300$) mass resolution mode. Sr, Pb, Th, and U were below detection limit for orthopyroxene. Data reduction was performed by first subtracting the average gas background from the ablation signal. Instrumental drift and ablation efficiency were then accounted for by normalizing to an initial measurement using an internal standard. In this case, we used the known concentration of an element for normalization (²⁵Mg) that had previously been determined using a JEOL JXA-8200 electron microprobe at the Massachusetts Institute of Technology. For the LA-ICP-MS analyses, elemental concentrations were quantified by generating calibration curves from multiple analyses of the three USGS glass reference materials BIR-1G, BHVO-2G and BCR-2G. Calibration curves included standards analyzed before and after each sample mount in order to correct for any secondary drift of the element/Mg ratio between standards and samples. These calibration

curves always produced correlation coefficients of $R^2 > 0.98$, which shows that instrumental drift between samples and standards was very minor. The uncertainty of individual trace element analyses are estimated to be ~10 % based on repeat analyses of USGS glasses BIR-1G, BHVO-2G and BCR-2G (Nielsen et al., 2014). Trace element concentrations in clinopyroxene and orthopyroxene in composite sample LN12-18 are reported in Table S3 and S4, respectively. REE concentrations in clinopyroxene in the nine ‘distal’ samples are also reported in Table 3.

3.3. Assumptions on the isotope model ages

The maximum age of melt-rock reaction was estimated using the Nd, Sr and Hf isotope composition and the Sm/Nd, Rb/Sr and Lu/Hf ratios of clinopyroxene in ‘distal’ lherzolite-websterite 06LI17 (Le Roux et al. 2009). ‘Distal’ lherzolite-websterite samples contain abundant websterite layers indicating that they have heavily reacted with the percolating melt. All clinopyroxenes in ‘distal’ samples (including 06LI17) show similar REE-depleted patterns (Fig. 2), indicating that they have all approached chemical equilibrium with the percolating melt. On the other hand, highly variable REE patterns are observed in ‘proximal’ samples located near the unpercolated harzburgitic protolith, due to trace element fractionation by small melt fractions (Fig.2 of Le Roux et al., 2009). Thus isotope data from ‘proximal’ samples (such as LN12-18) cannot be used for the isotope model age reconstructions. In addition, the Sr-Nd-Hf isotope composition of clinopyroxenes in 06LI17 plots near the MORB field (see Fig. 3 in Le Roux et al. 2009), consistent with the trace element composition of the percolating melt as calculated from nine ‘distal’ samples (see section 4.1.1), Clinopyroxenes in ‘distal’ lherzolite-websterite samples are also less likely to be strongly affected by diffusion after initial crystallization of websterites,

due to the lack of strong chemical gradients and trace element fractionations, as observed in ‘proximal’ harzburgites and lherzolites. Thus, isotope data from clinopyroxene in ‘distal’ lherzolite-websterite sample 06LI17 are ideal to calculate a maximum model age related to melt-rock reaction.

The vast majority of Sm, Nd, Rb, Sr, Lu, and Hf budgets reside in clinopyroxene as evidenced by Opx/Cpx partition coefficients of $\ll 0.1$ for most REE (Sun and Liang, 2014), with decreasing amount of REE in orthopyroxene as cooling goes. For example, assuming that REE are exclusively hosted in pyroxenes, orthopyroxene would typically host 2% of the total budget of Sm at 1200°C, and 0.5 % at 900°C (calculated using models of Sun and Liang, 2012; Yao et al., 2012). Thus, if the mantle contained 148 ppb Sm (McDonough and Sun, 1995), clinopyroxene would experience a 1.4 % increase of its Sm content from 1200°C to 900°C while orthopyroxene would experience a 74 % decrease of its Sm content from 1200°C to 900°C. Thus, sub-solidus diffusive equilibration of trace elements between orthopyroxene and clinopyroxene primarily affects orthopyroxene (Sun and Liang, 2014). With that, and the fact that the sample had been collected far away from large chemical gradients, we assume that clinopyroxene in ‘distal’ lherzolites recorded the isotope composition of the percolating melt and that Sm/Nd-Rb/Sr measured in clinopyroxene have not significantly changed since clinopyroxene crystallization from the melt. Heavy rare earth ratios such as Lu/Hf may be more affected by subsolidus reequilibration (Fig. 2).

3.4. Thermometry

The temperatures for harzburgite, lherzolite and websterite layers were calculated with a major element-based two-pyroxene thermometer (Brey and Kohler, 1990) using major elements analyses (Tables S1 and S2), and with a REE-in-two-pyroxene thermometer (Liang et al., 2013) using trace elements analyses (Tables S3 and S4). As demonstrated through numerical simulations (Yao and Liang, 2015), temperatures derived from the REE-in-two-pyroxene thermometer, which are closure temperatures of REE in the two-pyroxene system, are functions of cooling rate and grain size. Temperature inversions of the REE-in-two-pyroxene thermometer were performed for individual pairs of pyroxenes across cross section LN12-18. Closure temperatures of REE and major elements, are reported in Table S1 and S2. In order to insure the most accurate temperature calculations, we used pairs of near-adjacent pyroxenes where orthopyroxene and clinopyroxene were located at the same distance ($\pm 1\text{-}2\text{ mm}$) relative to the top of the layering ($z = 0$; see Fig. 1c). Because light REE are often altered by secondary processes and have very low abundances in orthopyroxene close to the limit of detection, they were excluded in the REE temperature calculations for our samples. Gd, Yb and Lu provided robust temperature calculations.

4. Results

4.1. Maximum age of melt-rock reaction

4.1.1. Composition of percolating melt

The REE composition of the percolating melt was calculated using clinopyroxene-melt partition coefficients (Sun and Liang, 2012) at melt temperatures relevant to the Earth's mantle (e.g., 1200°C-1400°C; Presnall et al., 2002) and REE concentrations in clinopyroxene from nine

248 'distal' lherzolites and websterites (Table S3). As an example temperature of 1250°C, we show
249 in Fig. 2 that melts in equilibrium with clinopyroxene in 'distal' lherzolites-websterites are
250 enriched in light rare earth elements (LREE) and resemble the rare earth element pattern of an
251 enriched MORB (E-MORB) melt (Gale et al., 2013). Equilibrium melts preserve their LREE
252 enrichment when compositions are calculated for a relevant range of mantle melt temperatures
253 (e.g., 1200°C-1400°C; Presnall et al., 2002). Heavy REE in the percolating melts calculated from
254 clinopyroxene compositions are greater than those in E-MORB by up to factors of 1.5. This
255 enrichment is attributed to elevated HREE abundances in clinopyroxene as a result of extensive
256 subsolidus re-equilibration (see Fig. 6 in Sun and Liang, 2014). We also calculated the
257 composition of the melt by using the whole-rock trace element concentrations of 'distal'
258 lherzolite-websterite sample 06LI17 (Table S5; obtained by ICP-MS solution at Geosciences
259 Montpellier as described in Godard et al., 2000), the modal proportions of that sample (22%
260 Opx; 24% Cpx), and the partition coefficients of trace elements between orthopyroxene,
261 clinopyroxene and melt at 1,250°C (Sun and Liang, 2012; Yao et al., 2012), assuming that all
262 trace elements are contained in pyroxenes. Accordingly, the enrichment in HREE is not present
263 in the calculated percolating melt using REE concentrations from whole rock data (Fig. 2). The
264 clinopyroxenes in the 34-cm layered harzburgite-lherzolite-websterite cross section LN12-18
265 collected for this study have similar MREE and HREE patterns than those in 'distal' lherzolites-
266 websterites (Fig. S1) because this 34-cm sample was collected near heavily percolated area (less
267 than 200 m. from 'distal' samples). However, it shows slightly more elevated LREE contents,
268 typical of 'proximal' lherzolites that are in contact with harzburgitic bodies (Le Roux et al.
269 2009). Thus, we strictly used the nine 'distal' samples to calculate the composition of the

percolating melt as they are the samples that are in closest chemical equilibrium to the percolating melt.

4.1.2. Isotope model ages

Melt-rock reaction ages are based on the assumption that the incoming melt was derived from an enriched MORB mantle reservoir, as discussed previously. The upper mantle has experienced long-term depletion in Nd over Sm, Rb over Sr and Hf over Lu, which caused the upper mantle to become more radiogenic for Nd and Hf isotopes and less radiogenic for Sr isotopes compared with bulk Earth (as represented by chondrites). The maximum age represents the time at which the percolating melt (assumed to be of the same isotopic composition as clinopyroxene in the ‘distal’ lherzolite-websterite) is no longer compatible with an isotope composition that could have been extracted from the upper mantle (i.e, out of the grey field in Fig. 4a and 4b). It is important to note that here we make the conservative inference that the percolating melt was extracted from the MORB mantle, which occupies a field rather than a single evolution curve. Even though the melt may have resembled an E-MORB (Fig. 2), it is not justified to assume a single mantle composition due to the relatively heterogeneous nature of the upper mantle. In our age model, we back-calculate the isotopic composition of the clinopyroxene that crystallized from the percolating melt as a function of time (black line in Fig. 4) and compare it with how the MORB mantle would have evolved over that time interval (grey field in Fig. 4). Once an age is reached where the clinopyroxene no longer overlaps with the realistic range of compositions for the upper mantle we infer that the melt could not have been extracted from the MORB mantle anymore, which provides a maximum age of the melt percolation. Because the clinopyroxene plots within the MORB field from present day until some time in the

Proterozoic, it follows that the percolating melt could have crystallized clinopyroxene any time between the maximum age and the exhumation age of the massif (black line in Fig. 4). Thus, the isotope model age can only provide a maximum age for melt-rock reaction.

Using the published Nd, Sr and Hf isotope data and Sm/Nd, Rb/Sr and Lu/Hf ratios of clinopyroxenes in the ‘distal’ lherzolite 06LI17 (Le Roux et al., 2009) we reconstruct the Nd, Sr and Hf isotope composition of the incoming melt as a function of age (black lines in Fig. 4; Table S6). For simplicity, we assume that the melt-rock reaction happened in one stage and formed both websterites and lherzolites (Le Roux et al., 2007). Although late intrusions of melts happened during exhumation (e.g. leading to the formation of rare amphibolite dikes that cross-cut the websterite and lherzolite foliations), there is no field evidence to support that layered spinel websterites in Lherz formed through multi-stage melt-rock reactions. However, if this was the case, then we would assume that clinopyroxenes only record the last stage of melt-rock reaction. It should be noted that the published isotope ratios in Le Roux et al. (2009) had been corrected to the age of exhumation, as it was assumed that melt-rock reaction and exhumation happened at a similar time. Here we report the raw values, uncorrected for exhumation. It should also be noted that two typos were present in the original Nd and Sr concentration data for the lherzolite clinopyroxene data (Le Roux et al., 2009). The correct raw values of all the isotope and concentration data are as follows (the numbers with an asterisk were the values that contained a typo): Nd = 4.21* ppm; Sm = 1.65 ppm, $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.513240, Rb = 0.034 ppm, Sr = 62.8* ppm, $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.702564, Lu = 0.26525 ppm, Hf = 0.904 ppm), and $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.283370.

The field representing the Nd isotope composition of modern MORB unaffected by plumes or subduction zone contamination has $\epsilon^{143}\text{Nd}$ values of 5-13 ($\epsilon^{143}\text{Nd} = 10000 * ((^{143}\text{Nd}/^{144}\text{Nd}_{\text{sam}} -$

$^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}})/^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}$, where Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ for CHUR were taken from Bouvier et al. (2008)) with E-MORB displaying values in the lower end of this range (Gale et al., 2013; Hofmann, 1997; Meyzen et al., 2007). By adopting a roughly linear Nd isotopic evolution for the mantle over the last ~ 2700 Ma, we construct a model for the MORB mantle that produces a range of $\epsilon^{143}\text{Nd} = 2-5$ at 2,700 Ma, in accordance with published estimates for the mantle at this time (Bennett, 2003). Our calculations show that the incoming melt would have passed below the inferred value for the most unradiogenic E-MORB at ~ 1,300 Ma (Fig. 4a). If we add 5 % uncertainty on the Sm/Nd ratio of the clinopyroxene, which is a conservative estimate of the 2 sigma standard error (2SE) based on reproducibility of Sm/Nd ratio in the nine samples of similar rare earth element (REE) compositions, then we obtain an age range between 1,000 Ma and 1,800 Ma. The upper end of this range provides a maximum age estimate of the time of the melt percolation. It should be noted that the calculated maximum model age is sensitive to the assumed minimum value for present day E-MORB. Our best age estimate uses $\epsilon^{143}\text{Nd} = 5$ in accordance with the most unradiogenic values observed at the South East Indian Ridge (Mahoney et al., 2002). Thus, we infer from the Nd isotope calculations that the melt percolation event at Lherz happened at the earliest ~ 1,800 Ma ago.

The field representing the Sr isotope composition of modern MORB unaffected by plumes or subduction zone contamination covers a range between $^{87}\text{Sr}/^{86}\text{Sr} = 0.702-0.704$ (Hofmann, 1997, Meyzen et al., 2007) with E-MORB displaying values in the upper end of this range (Gale et al., 2013; Hofmann, 1997). The Sr isotope evolution of the mantle is very poorly constrained due to the common alteration of Rb and Sr in ancient mantle derived rocks. Here, we choose a similar model to that of Nd isotopes for the MORB mantle with a linear radiogenic ingrowth since 2,700 Ma. We estimate the MORB mantle to have had a compositional range of $^{87}\text{Sr}/^{86}\text{Sr} = 0.701-$

0.702, with the lower value taken from the Sr isotope evolution model for MORB (Workman and Hart, 2005). The Rb/Sr ratio of clinopyroxene is very low and little radiogenic ingrowth of ^{87}Sr would have occurred in the lherzolite clinopyroxene even over the age of the Earth. Our calculations show that the incoming melt would have passed above the inferred value for the most radiogenic E-MORB at $\sim 2,000$ Ma (Fig. 4b). Uncertainty in the Rb/Sr ratio of the clinopyroxene makes no difference to this age because the Rb/Sr ratio is very low. However, the chosen value for $^{87}\text{Sr}/^{86}\text{Sr}$ of E-MORB at 2,700 Ma is the main controlling factor of the Sr model age. If we instead choose a value for E-MORB of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7015$ (i.e., change in the upper bound of the grey field; Fig. 4b), we obtain a maximum age of $\sim 1,600$ Ma (not shown). The age information provided by Sr isotopes, while consistent with the maximum Nd model age, is thus substantially more uncertain.

The field representing the Hf isotope composition of modern MORB unaffected by plumes or subduction zone contamination covers a range between $\epsilon^{176}\text{Hf} = 11\text{-}24$ (Gale et al., 2013; Hofmann, 1997; Meyzen et al., 2007) with E-MORB displaying values in the lower end of this range (Gale et al., 2013). Like for Nd isotopes, we adopt a roughly linear Hf isotopic evolution for the mantle over the last ~ 2700 Ma (Bennett, 2003) and construct a model for the MORB mantle that produces a range of $\epsilon^{176}\text{Hf} = 3\text{-}7$ at 2700 Ma (Fig. S2), in accordance with published estimates for the mantle at this time (Bennett, 2003). The Lu/Hf ratio of clinopyroxene in the lherzolite is similar to the integrated long-term average MORB reservoir and consequently the Hf isotope composition of the lherzolite clinopyroxene has broadly followed the same Hf isotopic evolution as the MORB mantle. Although this does not contradict our findings, no robust maximum age can be extracted based on Hf isotopes. In addition, Lu/Hf ratios were more

uncertain as they were likely affected by subsolidus reequilibration even in clinopyroxene, as opposite to Nd and Sm where subsolidus reequilibration is barely detectable in clinopyroxene.

Osmium isotopic data from Lherz mantle peridotites are more complex to interpret because it has been shown that on the cm-scale there can exist several generations of Os-rich sulfides, which reflect different melting and melt percolation events (Lorand et al., 2010). Hence, bulk peridotite Os isotope measurements in lherzolites-websterites from Lherz (Riches and Rogers, 2011) likely represent a mixture between 1) sulfides with unradiogenic Os isotope compositions from the unpercolated harzburgite protolith that record one or several ancient melt depletion events and 2) the incoming melt with more radiogenic values closer to the modern upper mantle or above (van Acken et al., 2010) that formed the websterites and lherzolites. Bulk analyses of Os isotopes in peridotites from Lherz (Riches and Rogers, 2011) are consistent with this interpretation, with lherzolites mostly displaying values of $^{187}\text{Os}/^{188}\text{Os} \sim 0.125\text{-}0.131$ combined with a relatively large range in $^{187}\text{Re}/^{188}\text{Os} = 0.1\text{-}0.5$ and harzburgites clustering around more unradiogenic values of $^{187}\text{Os}/^{188}\text{Os} \sim 0.113\text{-}0.12$ and lower $^{187}\text{Re}/^{188}\text{Os}$. There is a substantial scatter in these numbers, which is likely due to the 'nugget-effect' of Os-rich sulfides being inhomogenously distributed at the scale of the samples investigated. With these complexities in mind, it is difficult to extract age information based on Os isotopes. For example, lherzolites and harzburgites in Lherz display a broad correlation between $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$, which corresponds to an age of $\sim 1700\pm 400$ Ma (Reisberg and Lorand, 1995, Riches and Rogers, 2011). However, this age may equally be interpreted as a mixing line that does not bear any age information on the melt-rock reaction, unless most of the Re and Os in both lherzolites and harzburgites originate from the incoming melt.

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4.2. Minimum age of melt-rock reaction

Thirty-five closure temperatures were calculated using a major element-based two-pyroxene thermometer (Brey and Kohler, 1990) and a REE-in-two-pyroxene thermometer (Liang et al., 2013) on the 34-cm harzburgite-lherzolite-websterite cross-section LN12-18 (Table S1 and S2). At the scale of the 34-cm sample, we assume that the whole sample was exposed to the same temperature in the upper mantle. Major element closure temperatures for harzburgites, lherzolites and websterites average at $826 \pm 20^\circ\text{C}$ (2SE) (Fig. 5). REE closure temperatures for harzburgites, lherzolites and websterites average at $900 \pm 15^\circ\text{C}$ (2SE) (Fig. 5). Although some uncertainties are associated with major element-based thermometers (e.g., compositional zonations) and REE-based thermometers (e.g., uncertainty associated with low REE concentrations in Opx), REE closure temperatures are on average 74°C higher than closure temperatures recorded by major elements (Fig. 5). Importantly, both thermometers record temperatures that are well below the solidus of peridotites, indicating significant cooling since melt-rock reaction occurred.

We calculate the time scale for diffusive re-equilibration (Liang, 2014) of Gd, Yb, and Lu between clinopyroxene and orthopyroxene using partition coefficients of REE (Sun and Liang, 2012; Yao et al., 2012) and diffusion coefficients of REE (Cherniak and Liang, 2007; Van Orman et al., 2001, 2002) for a range of sub-solidus temperatures (from 1250°C to 900°C), and a pyroxene grain diameter of 2 to 3 mm, which is representative of the grain size in the peridotite-pyroxenite layering for that cross-section. Most clinopyroxenes and orthopyroxenes are 2 mm in size. Locally, larger pyroxenes can reach 3 mm. REE diffusion coefficients in clinopyroxene depend on ionic radius and increase from La to Lu (Van Orman et al., 2001, 2002), and

accordingly we extrapolate diffusion coefficients of Gd, Yb and Lu in clinopyroxene at given temperature and pressure of 1.5 GPa (Table S7). On the other hand, REE diffusion coefficients in orthopyroxene are not sensitive to ionic radius and can be described by a single Arrhenius equation (Cherniak and Liang, 2007). In order to calculate t_D at a given temperature and for a given element (Fig. 6), we used the following equation for time scale of diffusive re-equilibration (Liang, 2014):

$$t_D = \frac{1}{\beta \left(\frac{1}{L_A} + \frac{k_{AB}}{L_B} \right)} \left(\frac{L_A}{D_A} + \frac{L_B}{D_B} k_{AB} \right)$$

where β is a geometric factor and is 5 for a sphere, L_A and L_B are the radii of mineral A (e.g., orthopyroxene) and B (e.g., clinopyroxene), respectively, D_A and D_B are the diffusion coefficients of a given element in minerals A and B at a given temperature and a pressure of 1.5 GPa, and k_{AB} is the partition coefficient of a given element, at a given temperature, between mineral A and mineral B. We calculated the diffusive reequilibration times (t_D) for Gd, Yb, and Lu as those three elements were used to calculate REE closure temperatures. In Fig. 6, Yb was chosen as an example, as its diffusivity is intermediate between Gd and Lu.

The results illustrate the minimum amount of time it would take for orthopyroxene and clinopyroxene, in chemical disequilibrium due to subsolidus cooling, to diffusively reequilibrate their REE and record a given subsolidus temperature. In Fig. 6, we show that t_D rapidly increases with decreasing temperature, as diffusion of REE between orthopyroxene and clinopyroxene is drastically slowed down as cooling goes. For example, for a pyroxene diameter of 2 mm, it takes ~ 70 Ma for orthopyroxene and clinopyroxene to diffusively re-equilibrate their Yb such that they can record a temperature of 1000°C. On the other hand, for the same grain size, it takes at

least ~ 1,400 Ma for orthopyroxene and clinopyroxene to diffusively re-equilibrate their Yb such that they can record a temperature of 900°C. For a pyroxene size of 3 mm, it takes at least 1,900 Ma for orthopyroxene and clinopyroxene to diffusively re-equilibrate their Yb such that they can record a temperature of 900°C ($\pm 15^\circ\text{C}$). For a given element, the larger the grain and the lower the temperature, the longer the process of diffusive re-equilibration takes. Although we will consider the average REE closure temperature of 900°C ($\pm 15^\circ\text{C}$) obtained with 35 samples for the remaining of the discussion, we should point out that a higher temperature of 915°C (within 2SE) on a pyroxene size of 2 mm would be reached after ‘only’ ~ 900 Ma.

5. Discussion

5.1. Dating layered websterite formation

Assuming that the lherzolites and layered websterites in Lherz formed at the same time through melt-rock reaction (Le Roux et al., 2009; Le Roux et al., 2007; Le Roux et al., 2008) between an E-MORB melt and a harzburgitic lithospheric mantle, we show that the maximum age for melt-rock reaction can be calculated using the Nd isotope compositions and Sm/Nd ratio of clinopyroxene in ‘distal’ samples, equilibrated with the percolating melt. Our calculations show that the incoming melt would have passed below the inferred $\epsilon^{143}\text{Nd}$ value for the most unradiogenic E-MORB at 1,300 $\pm$ 500 -/300 Ma, which corresponds to the maximum age of melt percolation that produced both the lherzolites and the layered websterites (Fig. 4). Evidence based on Sr, Hf and Os isotopes is less well constrained, but equally compatible with age constraints from Nd isotopes.

In parallel, we show that a minimum age for melt-rock reaction and formation of layered pyroxenites can be calculated using REE closure temperatures and diffusion modeling for subsolidus cooling (Fig. 6). Because of the slower diffusion rates of REE in minerals compared to most major elements, the REE-based thermometer records earlier thermal events than the major element-based thermometers for samples from cooling environments (Dygert and Liang, 2015; Liang et al., 2013; Yao and Liang, 2015). Although it may not be surprising to obtain low closure temperatures (800-900°C) in mantle lithosphere using a major-element based thermometer, it takes considerably longer to reset REE through diffusive re-equilibration at subsolidus temperatures. Assuming that the harzburgitic protolith, newly-formed lherzolites and newly-formed layered websterites must have locally reached the temperature of the percolating melt ($> 1200^{\circ}\text{C}$) during melt-rock reaction, REE closure temperatures constrain how much time is necessary for pyroxenes to chemically re-equilibrate down to $\sim 900^{\circ}\text{C}$. REE closure temperatures are lower than what has been calculated for most ophiolitic and ridge peridotites worldwide (Dygert and Liang, 2015), as exhumation and cooling rates in those environments can be relatively fast. However they are in agreement with previous estimates of REE temperatures from Lherz, even though previous temperatures were calculated using pairs of orthopyroxene and clinopyroxene that were not near-adjacent and were calculated from other parts of the massif (Dygert and Liang, 2015). Closure temperatures of REE in Lherz are similar to what has been calculated for some sub-continental xenoliths, equilibrated for hundreds of millions of years in the shallow upper mantle (Liang et al., 2013). Assuming that all REE exchanges have stopped at the time of exhumation due to low temperatures in the crust, ($< 800^{\circ}\text{C}$; Sautter and Fabriès, 1990), the minimum age for melt-rock reaction, for 2-mm diameter pyroxenes, is $\sim 1,500$ Ma (1,400 Ma + exhumation age of 104 Ma). For 3-mm diameter pyroxenes, the minimum age of

melt-rock reaction would be close to the maximum age constraints defined by Nd isotopes (~1,800 Ma). Therefore, the melt-rock reaction that formed layered websterites in the Lherz massif happened at the earliest at ~ 1,500 Ma and at the latest at ~ 1,800 Ma during the mid-Proterozoic (Fig. 7) and is strongly disconnected from the exhumation event at 104 Ma.

5.2. Layered websterites and the pyroxenite cycle

The novel combination of isotope model ages, high-resolution REE variations in pyroxenes, REE closure temperatures and time-scale of diffusive re-equilibration shows that the layered websterites of Lherz formed more than a billion years before the exhumation process. Therefore, melt-rock reactions that produced the websterite layers were clearly disconnected from the process of exhumation. Multiple generations of websterites in other massifs, along with the evidence for ancient melt-rock reactions in Lherz, indicate that melt-rock reactions happen episodically or continuously in the mantle, not just before exhumation, and that refertilization processes are likely ubiquitous. In general, this does not exclude that layered websterites could form up until exhumation of a massif, which could be the last thermal event susceptible to produce layered websterites. In a ridge setting where websterites have also been observed (Dantas et al., 2007; Warren, 2016), there may not be enough time to differentiate between timing of exhumation and the timing of melt-rock reaction, compared to a subcontinental environment where mantle rocks could have hundreds of millions of years to diffusively reequilibrate. Layered websterites may be currently present in the shallow lithospheric mantle in most tectonic environments. Previous studies have suggested that the formation of layered reaction products would be favored by the presence of sharp thermal boundaries such as the

lithosphere-asthenosphere transition (e.g., Lenoir et al., 2001), or solid compaction processes associated with localized deformation (Holtzman et al., 2003; Le Roux et al., 2008; Soustelle et al., 2014; Spiegelman et al., 2001). Although layered websterites worldwide have variable compositions and mineral assemblages, several studies have suggested that layered pyroxenites may represent hybrid pyroxenites, i.e., formed through multi-stage reaction between eclogite-derived melt and the peridotite mantle (e.g., Borghini et al., 2016; Rosenthal et al., 2014; Sobolev et al., 2005), and probably variable proportions of peridotite-derived melt. That general process is illustrated in Fig. 8. In Lherz, percolation of enriched MORB-like melts may also indicate contribution from eclogite-derived melts through a multi-step melting-reaction process.

6. Conclusions

Layered websterites are found in many orogenic and ophiolitic peridotites and their formation is often ascribed to melt infiltration and melt-rock reaction processes, accompanied by variable amount of deformation. Here we have investigated the timing of formation of layered websterites formed by melt-rock reaction in the Lherz massif (France). Using a novel combination of isotope model ages, high-resolution REE variations in pyroxenes, REE closure temperatures and time-scale of diffusive re-equilibration, we showed that layered websterites formed between ~ 1,500 Ma and ~ 1,800 Ma, and are clearly disconnected from the process of exhumation at 104 Ma. We argue that if the age of exhumation and the age of formation of layered websterites can be disconnected, such as in Lherz and other orogenic and ophiolitic massifs, ubiquitous layered websterites are not necessarily linked to local exhumation processes, but are rather representative of ubiquitous, large-scale melt infiltration processes in the

lithospheric mantle. Our novel approach can be applied to layered websterites from other tectonic environments to further understand the formation of those ubiquitous layers.

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Figure legends

Fig. 1. Parallel layers of websterites in the Lherz Massif, formed through melt-rock reactions in composite sample LN12-18 (a) Location of the samples on the outcrop. (b) Position of the websterite layers within the peridotite matrix. (c) Lithological variations across the 34-cm peridotite-websterite layering and position of thick sections across the layering.

Fig. 2. Solid brown lines are rare earth element concentrations normalized to chondrites (McDonough and Sun, 1995) in clinopyroxene in lherzolites and websterites in equilibrium with percolating melts ('distal' samples), and dotted brown lines are rare earth element (REE) concentrations of percolating melts, in equilibrium with clinopyroxene in 'distal' samples, calculated using Sun and Liang (2012) at 1250°C. 'Subsolidus reequilibration' illustrates the effect of subsolidus cooling on heavy rare earth elements. Solid blue line is whole-rock concentrations of REE in 06LI17, and dotted blue lines are calculated REE concentrations of percolating melts in equilibrium with whole-rock concentrations at 1250°C, showing that results from REE in clinopyroxene and whole-rock are consistent.

Fig. 3. High-resolution variability of Yb in clinopyroxene and orthopyroxene across the 34-cm cross section LN12-18 (Tables S3 and S4). Colors of lithologies are the same as in Fig. 1.

Fig. 4. (a) Epsilon Nd (ϵ Nd) and (b) $^{87}\text{Sr}/^{86}\text{Sr}$ in clinopyroxene today (green symbol) calculated back in time (solid black line) to estimate the maximum age of clinopyroxene crystallization from an E-MORB melt (red symbol). The grey field represents the isotope variability of MORB and E-MORB field. A 5 % uncertainty on the Sm/Nd ratio (discussed in the text) provides a range for the maximum age (orange symbols). Details of calculations are available in Table S6.

Fig. 5. Comparison of closure temperatures of REE in pyroxenes (Liang et al., 2013), calculated using the REE chemistry of clinopyroxene and orthopyroxene (Tables S3 and S4), and closure temperatures of major elements in pyroxenes (Brey and Kohler, 1990), calculated using the major element chemistry of orthopyroxene and clinopyroxene (Tables S1 and S2), in Lherz ultramafics. The 1:1 line shows that REE closure temperatures are on average higher than major element closure temperatures due to slower diffusive reequilibration of REE between orthopyroxene and clinopyroxene. Temperature calculations are available in both Tables S1 and S2.

Fig. 6. t_D Yb is the timescale of Yb diffusive re-equilibration between orthopyroxene and clinopyroxene at a given temperature. Black dotted line shows the minimum time necessary for Yb to reequilibrate at 900°C for 2-mm diameter pyroxenes (like in composite sample LN12-18). Dotted blue line represents the average REE closure temperature for all layers, and blue field represents 2 sigma standard error on the average (15°C).

Fig. 7. Exhumation age (in red) is added to t_D to determine the minimum age of melt-rock reaction that produced layered websterites in Lherz. The minimum age is calculated from REE closure temperatures and time scale of diffusive re-equilibration of REE between pyroxenes (in green), and the maximum age is obtained considering Nd isotope model age constraints and the composition of the percolating melt (in blue). The grey field thus constrains the timing of formation of layered websterites.

Fig. 8. Mantle pyroxenites: from asthenosphere to lithosphere. Schematic cycling of pyroxene-rich lithologies from subduction of eclogites to exhumation of ubiquitous layered lithospheric websterites based on this study and extensive previous literature (e.g., Lambart et al., 2012).

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8