Isotopic decoupling during porous melt flow: A case-study in the Lherz peridotite

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ABSTRACT

Most peridotite massifs and mantle xenoliths show a wide range of isotopic variations, often involving significant decoupling between Hf, Nd and Sr isotopes. These variations are generally ascribed either to mingling of individual components of contrasted isotopic compositions or to time integration of parent-element enrichment by percolating melts/liquids, superimposed onto previous depletion event(s). However, strong isotopic decoupling may also arise during porous flow as a result of daughter-elements fractionation during solid–liquid interaction. Although porous flow is recognized as an important process in mantle rocks, its effects on mantle isotopic variability have been barely investigated so far. The peridotites of the Lherz massif (French Pyrenees) display a frozen melt percolation front separating highly refractory harzburgites from refertilized lherzolites. Isotopic signatures observed at the melt percolation front show a strong decoupling of Hf from Nd and Sr isotopes that cannot be accounted for by simple mixing involving the harzburgite protolith and the percolating melt. Using one dimensional percolation–diffusion and percolation–reaction modeling, we show that these signatures represent transient isotopic compositions generated by porous flow. These signatures are governed by a few critical parameters such as daughter element concentrations in melt and peridotite, element diffusivity, and efficiency of isotopic homogenization rather than by the chromatographic effect of melt transport and the refertilization reaction. Subtle variations in these parameters may generate significant inter-isotopic decoupling and wide isotopic variations in mantle rocks.

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1. Introduction

Mantle rocks that outcrop at the Earth’s surface provide a direct source of information on the composition and evolution of the Earth’s mantle. Isotopes systematics observed in most peridotite massifs (Reisberg and Zindler, 1986; Downes et al., 1991; Pearson and Nowell, 2004) and mantle xenoliths (Deng and McDougall, 1992; Witt-Eickschen and Kramm, 1997; Bizimis et al., 2003; Wittig et al., 2007) show a wide range of variations compared with single suites of mantle-derived lavas. Some of the isotopic variations observed in peridotite massifs are correlated with lithologies, e.g. pyroxenites vs. peridotites (Reisberg and Zindler, 1986; Pearson and Nowell, 2004) and have been ascribed to convective mingling of subducted material with pristine material (Allègre and Turcotte, 1986; Becker, 1996). Other, small scale heterogeneities are ascribed to isotopic enrichment by metasomatizing fluids/liquids superimposed onto ancient depletion due to melt extraction (Downes et al., 1991; Bizimis et al., 2003; Wittig et al., 2007). The time integration of both depletion and enrichment of parent elements is often considered as the primary cause of isotopic variations in lithospheric peridotites.

However, few studies have tackled the relationships between isotopic variations and metasomatic processes (e.g., Ionov et al., 2002; Bodinier et al., 2004). Therefore, the mechanisms of isotopic enrichment and inter-isotopes decoupling during mantle metasomatism are still barely understood. Additionally, the “instantaneous” (as opposed to “time-integrated”) effect of melt transport on isotopes systematics is usually neglected, although it may theoretically generate drastic fractionation of daughter elements from different isotopic systems (Navon and Stolper, 1987). Further complexity may also arise from solid–liquid disequilibrium during fluid/melt-rock interaction. Van Orman et al. (2001) showed that REE (Rare-Earth Elements) diffusion in clinopyroxene at magmatic temperatures may be slower than first envisioned. For instance, Sneeringer et al. (1984) obtained a diffusion rate of ~5·10−15 cm² s⁻¹ for Sm in diopside at 1250 °C and 1.4 Gpa while Van Orman et al. (2001) showed that Yb, one of the fastest REE, did not diffuse faster than ~6·10−16 cm² s⁻¹ at the same pressure–temperature conditions. The high mantle temperature and the relatively slow rate of mantle melting may not guarantee isotopic equilibrium between the solid residue and the extracted molten fractions when the mantle source is isotopically heterogeneous. In the lower temperature conditions of the lithosphere–asthenosphere transition, diffusion processes may be even slower, and therefore chemical and isotopic equilibrium between minerals and percolating melts may not be reached.
Recent studies in the Lherz massif, the type-locality of lherzolites exposed in the French Pyrenees, suggest that the Lherz lherzolites formed through a near-solidus refertilization reaction between a harzburgitic protolith and ascending partial melts (Le Roux et al., 2007). The transition zone between the remnants of the harzburgitic protolith and the refertilized material represents a frozen melt-percolation “front”, tens of meters wide that moved through the subcontinental mantle lithosphere. Thus, the massif offers a unique opportunity to trace Hf, Nd and Sr isotopic variations related to melt transport. We used a one-dimensional percolation–diffusion model (Vasseur et al., 1991) modified to include isotopic homogenization and a percolation–reaction model (Vernières et al., 1997) to assess the effects of mineralogical reactions on isotopic variations. We show that transient, decoupled, isotopic signatures may develop in a melt percolation front. These signatures are highly sensitive to parameters such as daughter-element concentrations in peridotite and melt, element diffusivity, mineral grain size and efficiency of isotopic re-equilibration. The variations observed in the Lherz peridotites are more readily governed by diffusional peridotite-melt disequilibrium than by the chromatographic effect of melt transport and the refertilization reaction.

2. Background and sampling

The Lherz massif is one of the largest peridotite massifs in the Pyrenees (France), exhumed from the mantle around 105 Ma ago (Henry et al., 1998) and exposed within sedimentary basins of Cretaceous age. Pyrenean peridotites usually outcrop embedded in metamorphized carbonate sediments of Jurassic to Aptian age (Golberg and Leyreloup, 1990) scattered in small groups along the North Pyrenean Fault (Monchoux, 1971; Fabriès et al., 1991; Fig. 1a). The Lherz massif is mostly constituted of fertile spinel lherzolites associated with websteritic layers, intermingled with elongated bodies of depleted spinel harzburgites (Avé Lallemant, 1967; Conquéry, 1978; Fabriès et al., 1991; Le Roux et al., 2007; Fig. 1b).

Recent work yielded convergent structural and geochemical evidence demonstrating that the melt-extraction hypothesis, which regards depleted harzburgites as derived through partial meting of the fertile lherzolites, was not consistent with structural and chemical observations (Le Roux et al., 2007). Harzburgites bodies show a consistent sub-horizontal foliation throughout the massif that is crosscut by the Iherzolite foliation and the websteritic layering. This suggests that the harzburgite bodies once formed a single continuous unit and that the deformation of harzburgites predates the formation of the lherzolites and websterites. Microstructural and petrophysical data indicate that the deformation of the lherzolite–websterite suite was enhanced by the presence of melts. By feedback effect, larger melt fractions favored strain localization and larger strain favored melt percolation through a higher dynamic porosity (Le Roux et al., 2008). Besides, major and minor elements correlations, as well as the association of LREE-enriched harzburgites and LREE-depleted lherzolites, are not consistent with partial melting, but can be explained by melt-rock reaction. Thus the Lherz lherzolites probably formed during a refertilization episode via a near-solidus reaction at the expense of a harzburgite protolith (Le Roux et al., 2007). Therefore the transition zone between the harzburgitic protolith and the refertilized material represents a frozen, anastomosed, melt-percolation “front”, tens of meters wide that moved through the subcontinental mantle lithosphere.

Fig. 1. (a) Distribution of the Pyrenean peridotite bodies along the North Pyrenean Fault (NPF), from Lagabrielle and Bodinier (2008) after Choukroune and Mattauer (1978). 1: Oligocene and post-Oligocene sediments; 2: Mesozoic and Eocene sediments; 3: Paleozoic basement; 4: area of LP-HT Pyrenean metamorphism; 5: lherzolite bodies; 6: granulites; 7: main thrusts external zones; 8: North Pyrenean Fault. (b) Harzburgites and lherzolites intermingling in the Lherz massif (Le Roux et al., 2007); the location of the sampling sites are indicated on the map, 1: distal lherzolite; 2: profile through a contact; 3: distal harzburgites. (c) Detailed sampling site 2 through a harzburgite-lherzolite contact.
Within the transition zone we sampled 8 harzburgites and 5 lherzolites along a ~10 m profile across one contact between harzburgite and lherzolite (Fig. 1c). The new samples come from the same locality than samples from Section 2 in Le Roux et al. (2007). The sampled zone is not cross-cut by dykes and/or veins related to the alkaline magmatism that affected the Lherz massif during Cretaceous time. Three ‘distal’

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Table 1

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The associated 87Rb/86Sr, 143Sm/144Nd and 176Hf/177Hf isotope ratios in the 16 clinopyroxenes separate from a harzburgite–lherzolite transition zone in the Lherz massif as well as in distal samples (06LI15: harzburgite protolith; 06LI17 distal lherzolite), obtained by TIMS and MC-ICP-MS techniques at the GEMOC ARC National Key Centre (Australia).
peridotites have also been sampled, outside of the transition zone at more than 15 m from a contact, to characterize the lithospheric protolith and the refertilized mantle.

We present here the Hf, Nd and Sr isotopic compositions of clinopyroxenes separates, considered to have similar isotopic signatures to the whole-rocks, and their rare-earth elements compositions obtained during this study.

3. Samples preparation and analytical methods

Rare Earth Elements (REE) were obtained by Laser ablation inductively coupled plasma-mass spectrometer (LA-ICP-MS) at GEMOC ARC National Key Centre (Australia), using an Agilent 7500 ICPMS coupled with a frequency quintupled Nd:YAG UV laser from New Wave/Merchantek laser microprobes. Ablation was performed under a pure He atmosphere, with a spot size of 70 µm, energy density of 10 J cm⁻² and the repetition rate was set at 10 Hz. The oxide production was kept low (²⁴⁸ThO/²³²Th < 1%). Data reduction was carried out using the GLITTER software (Van Achtebergh et al., 2001). The CaO content of clinopyroxenes (Cpx), obtained by electron microprobe (Cameca SX 100, GEMOC ARC National Key Centre), was used as internal standard. Data in Table 1 are averages of “n” analyses of different Cpx grains from the same sample.

Aliquots of the crushed samples were ground in agate mortars to produce whole-rocks powders. Cpx fractions were obtained for the same samples by magnetic pre-concentration (using a Frantz magnetic separator), further purification was achieved through careful hand-picking under a binocular microscope. The final 16 pure clinopyroxene fractions (weights ranging between 102 to 222 mg) have been leached prior to dissolution to remove possible contamination from grain surfaces and cracks. Cpx mineral were leached in 2 N two-bottle distilled HCl for 30 min in an ultrasonic bath and then rinsed three times with MQ-H₂O. This procedure was repeated twice.

Hf, Nd and Sr isotopes analyses, including samples dissolution, chemical separation and measurements were carried out at the GEMOC ARC National Key Centre (Macquarie University, Australia). Chemical separation of Sr and Nd were performed using standard dissolution and column procedures described by Mukasa et al. (1991) and by Pin and Zalduegui (1997) for Nd-specific columns. Hf chemical separation was carried out following the protocol of Blichert-Toft (2001). The sixteen Sr and nine Nd isotopic ratios of clinopyroxene separates were obtained on a Thermo Finnigan Triton thermal ionization mass spectrometer (TIMS). ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios were corrected for instrumental mass fractionation by normalizing to ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219, respectively. Seven replicate analyses of the BHVO-2 standard yielded ⁸⁶Sr/⁸⁶Sr of 0.703491 ± 8 (2SD; typical internal precision was about 5·10⁻⁶) and ¹⁴³Nd/¹⁴⁴Nd of 0.512997 ± 5 (2SD; typical internal precision was about 4·10⁻⁶). These values are well within the accepted-published values (Weis et al., 2005).

The sixteen Hf and seven Nd isotopic ratios of clinopyroxene separates were obtained on a Nu Plasma high resolution multicollector inductively-coupled plasma mass spectrometer (MC-ICP-MS). All measured Hf isotopic ratios were corrected for W and Ta, and Lu and Yb interference at masses 180 and 176, respectively, by monitoring the isotopes ¹⁸⁲W, ¹⁸¹Ta, ¹⁷⁵Lu, and ¹⁷⁵Yb, and normalized for mass fractionation to ¹⁷⁷Hf/¹⁷⁷Hf of 0.7235 using an exponential law. In order to assess the daily performance of the MC-ICP-MS, JMC475 (≈50 ppb) and JMC321 (≈50 ppb) were used as internal standards for Hf and Nd respectively and yield (¹⁷⁷Hf/¹⁷⁷Hf)₉ᵐᵦₛ = 0.282173 ± 15 (2SD; n = 18; typical internal precision is ca 3·10⁻⁶) and (¹⁴³Nd/¹⁴⁴Nd)₉ᵐᵦ₄ = 0.511088 ± 20 (2SD; n = 5; typical internal precision is ca 5·10⁻⁶). Four standards BHVO-2 gave a (¹⁷⁷Hf/¹⁷⁷Hf) of 0.283107 ± 20 (2SD; typical internal precision is ca 8·10⁻⁶) and (¹⁴³Nd/¹⁴⁴Nd) of 0.512961 ± 9 (2SD; typical internal precision is ca 6·10⁻⁶). These values are well within the accepted-published values (Barrat and Nesbitt, 1996; Blichert-Toft and Albarede, 1997; Weis et al., 2005). Procedural blanks were as follows: [Sr]blank = 139 ± 61 pg (n = 2); [Nd]blank = 26 pg (n = 1); [Hf]blank = 64 ± 31 pg (n = 3). The results are given in Table 1.

4. Results

REE obtained in clinopyroxenes from the sixteen peridotites sampled for this work (Table 1) show strongly depleted, U-shaped patterns in distal harzburgite bodies with L₁₋₂ = 0.5 and (La/Sm)₁₋₂ (normalized to chondrites after Sun and McDonough, 1989) and classic, N-MORB, REE pattern in the distal lherzolite (L₁₋₂ = 2.3; (La/Sm)₁₋₂ ≈ 0.3), as observed in orogenic lherzolites worldwide (McDonough and Frey, 1989). At the contact, lherzolite and harzburgite show more Light-REE-enriched clinopyroxenes than their distal counterparts, especially in harzburgites which display strong enrichment in LREE relative to HREE (HRREE) and/or Medium REE (MREE) with L₁₋₂ up to 29 and (La/Sm)₁₋₂ ~ 3 (Fig. 2). These patterns are similar to the representative REE patterns at the massif-scale obtained on more than 50 samples in Le Roux et al. (2007). Thus the harzburgite–lherzolite contact sample for this study can be considered as a representative transition zone between harzburgites and lherzolites. The association of LREE-enriched harzburgites with LREE-depleted lherzolites observed at the harzburgite–lherzolite contact in the Lherz massif are actually predicted by theoretical modeling of melt-consuming reactions combined with melt transport (Vernières et al., 1997) and were attributed to small melt fractions residual after the refertilization reaction which migrated in the harzburgite protolith several meters ahead of the main reaction front (Le Roux et al., 2007). We consider that the U-shaped patterns observed in the distal harzburgites are related to an older metasomatic event, distinct from the refertilization episode that affected the Lherz peridotites (Le Roux et al., 2007). The models presented in this study aim to reproduce the effect of the refertilization episode.

Hf, Nd and Sr isotopic compositions of the 16 clinopyroxene separates from harzburgites and lherzolites of the Lherz massif are presented in Fig. 3. The isotopic signatures of the Lherz peridotites are widely scattered. Hf isotopes describe a large range of variations (2<εHf <214) that encompasses a significant part of the variability seen in cratonic and off-craton peridotites worldwide (Fig. 3a). ⁸⁷Sr/⁸⁶Sr ratios also vary between 0.702562 and 0.703276 and εNd ranges between −1.7 and 8.8 (Fig. 3b). The harzburgitic protolith and the distal refertilized lherzolites have distinctive isotopic signatures that define two different poles. One is a highly refractory lithosphere...
Al₂O₃ wt.% has been ascribed to an old (Proterozoic) depletion event with partial melting (Downes et al., 1991; Bodinier and Godard, 2003). Ocean-Island Basalts with partial melting (Downes et al., 1991; Mukasa et al., 1991; Fig. 3), suggesting a no visible harzburgites are isotopically comparable to the distal Lherz depleted signature (Fig. 2). Other Pyrenean lherzolites that contain variations of TCHUR Hf model ages in harzburgitic samples, uncertainty age (Alard et al., Submitted for publication). However, giving the model ages (Reisberg and Lorand, 1995) and ~2.5 Ga in-situ Os model slightly younger than the ~2.2 Ga previously published Re depletion Nd (⁹⁷Sr/⁸⁶Sr=0.703046). Calculations of the TCHUR Hf model age gave a value of –2.1 Ga on the protolith sample (O6L115), slightly younger than the –2.2 Ga previously published Re depletion model ages (Reisberg and Lorand, 1995) and ~2.5 Ga in-situ Os model age (Alard et al., Submitted for publication). However, giving the variations of TCHUR Hf model ages in harzburgitic samples, uncertainty on this age is probably high. The ‘distal’ harzburgitic sample which combines a U-shaped, highly REE-depleted signature (Fig. 2) and the most enriched isotopic composition is considered to be the closest to the depleted protolith before refertilization. The two pole is represented by a distal refertilized lherzolite characterized by a MORB-like isotopic signature (ε_Hf=18; ε_Nd=9; ⁸⁷Sr/⁸⁶Sr=0.702562) and a LREE-depleted signature (Fig. 2). Other Pyrenean lherzolites that contain no visible harzburgites are isotopically comparable to the distal Lherz lherzolite (Downes et al., 1991; Mukasa et al., 1991; Fig. 3), suggesting a similar origin by regional magmatic refertilization. Harzburgites and lherzolites from the transition zone differ markedly from the distal ones with respect to their isotopic signatures. Their compositions plot close to the field of intraplate basalts (Ocean-Island Basalts and HIMU) and a simple mixing between the two poles defined by the distal peridotites particularly fail to account for their Hf–Nd isotopic signatures (Fig. 3).

5. Discussion

5.1. Contrasted isotopic compositions of lherzolites and harzburgites in the Pyrenees

Previous works have revealed that fertile lherzolites and depleted harzburgites in eastern Pyrenean peridotites show markedly distinct Os–Sr–Nd isotopic signatures (Downes et al., 1991; Reisberg and Lorand, 1995; Burnham et al., 1998). The positive correlation of ¹⁸⁷Os/¹⁸⁸Os with Al₂O₃ wt.% has been ascribed to an old (Proterozoic) depletion event (Reisberg and Lorand, 1995; Burnham et al., 1998). However, ⁸⁷Sr/⁸⁶Sr and ¹⁴⁳Nd/¹⁴⁴Nd show, respectively, negative and positive correlations with Al₂O₃ wt.% in whole-rocks, a feature which is not consistent with partial melting (Downes et al., 1991; Bodinier and Godard, 2003). Downes et al. (1991) proposed that the lherz harzburgites were selectively percolated by enriched melts whereas Bodinier and Godard (2003) interpreted them as lithospheric strips incompletely mixed with pristine asthenospheric lherzolites during thermo-mechanical erosion of the lithosphere by upwelling mantle. Recently, Le Roux et al. (2007) suggested that the refertilization scenario was the most likely to explain, at the same time, the positive correlation of ¹⁸⁷Os/¹⁸⁸Os vs. Al₂O₃ and the negative and positive correlations of ⁸⁷Sr/⁸⁶Sr and ¹⁴⁳Nd/¹⁴⁴Nd, respectively, vs. Al₂O₃.

The Nd and Sr isotopic variations observed in this study, from the harzburgitic protolith to the refertilized lherzolites, are consistent with previously published data in the Pyrenees (Downes et al., 1991). We obtained a Nd–Sr negative correlation which can be roughly accounted for by mixing between a low-Nd/high-Sr harzburgite protolith and a melt in equilibrium with the high-Nd/low-Sr distal lherzolite (Fig. 3b). However, at the harzburgite–lherzolite contacts, the Hf isotopes are strongly decoupled from Nd (Fig. 3a) and Sr (not shown). In contrast with the Nd–Sr isotopic covariation, the Hf–Nd isotopic signatures observed at the harzburgite–lherzolite contact cannot be accounted for by mixing between the harzburgite protolith and a melt in equilibrium with the distal lherzolites (Fig. 3a). In a mixing scheme, these isotopic signatures would require a third, undiagnostic Hf–Nd component. However, this would necessitate the circulation of intraplate-type melt strictly confined to the sharp and convoluted contact between harzburgites and lherzolites, which is very unlikely according to chemical and structural constraints. A more likely alternative is that these isotopic signatures formed at the melt percolation front through a particular chemical/physical process that led to the decoupling of Hf from Nd and Sr.

5.2. Modeling of isotopic reequilibration during melt percolation

We have evaluated the influence of melt percolation on isotopic reequilibration between peridotite and an infiltrated melt using a one-dimensional percolation-diffusion model (Vasseur et al., 1991) modified to include isotopic homogenization. The model incorporates the effects of chemical diffusion, critical distance of isotopic homogenization, melt velocity, height of the percolating column and grain
size. It assumes instantaneous solid–liquid equilibrium at the surface of mineral grains, considered to be spherical, and chemical diffusion within the grains, from surface to core. Isotopic equilibrium between fluid and solid phases is governed by the mass-balance equation of isotopic homogenization at the scale of critical volumes. The critical volume of isotopic homogenization is defined as the volume of percolated peridotite in which melt and matrix have reached isotopic equilibrium during the critical time of percolation (i.e., the times it takes for the melt to reach the top of the column). In addition, a percolation-reaction model (the “plate model” of Vernières et al., 1997) has also been used to evaluate the effects of the refertilization reaction on isotopic reequilibration during melt percolation. The plate model assumes instantaneous solid–liquid equilibrium between the whole mineral matrix and the melt.

Isotopic reequilibration between a rock and a disequilibrium percolating melt involves four distinct processes: (a) advective transport of the elements by interstitial melt; the chromatographic theory of Navon and Stolper (1987) predicts that incompatible elements in the matrix reequilibrate with the melt at lower melt-rock ratios than more compatible elements, producing extreme chemical fractionations when mineral-melt diffusional exchange is rapid; (b) chemical diffusion within the minerals and the melt; diffusion rates vary according to elements and pressure–temperature conditions; (c) isotopic homogenization of rock volumes by self-diffusion, which is effective even in the lack of chemical potential gradient (e.g. when the percolating melt and the peridotite have reached chemical equilibrium); (d) chemical reaction between the rock and the infiltrating melt that changes the mineralogical composition of the rock and/or the melt fraction.

A detailed parameterization was carried out to assess the influence of the main percolation–diffusion model parameters on the covariation of Hf, Nd and Sr isotopic compositions in a harzburgite column percolated by a melt in equilibrium with the distal Iherzolites. The parameters used for modeling are compiled in Table 2. The protolith was very likely heterogeneous; for modeling we took the most extreme composition characterized by the highest \(^{176}\text{Hf}/^{177}\text{Hf}\) and \(^{87}\text{Sr}/^{86}\text{Sr}\) and the lowest \(^{143}\text{Nd}/^{144}\text{Nd}\) values in the studied harzburgites. As isotopic composition for the melt, we took that of the distal, refertilized Iherzolite. This sample is comparable to other Pyrenean Iherzolites unrelated to harzburgites (Downes et al., 1991) and is therefore considered to be equilibrated with the fertilizing infiltrated melt. In all experiments the length of the percolation column has been fixed at 100 m. This length corresponds to the typical distance in the Lherz massif between the distal harzburgites, which represents the protolith before percolation, and the distal Iherzolites, considered to be fully equilibrated with incoming, fertilizing melt. Mineral/melt partition coefficients are from Blundy et al. (1998), Lee et al. (2007) and McDade et al. (2003).

For simplicity, the chemical diffusivities in solid phases, \(d\), were considered to be identical for all minerals. Extrapolated at 1250 °C and 1.5 GPa from the experimental data of Van Orman et al. (2001), the diffusion rate of Nd was fixed at \(3.4 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}\). The diffusion of Hf was estimated from its ionic radius and charge, yielding a diffusion rate of \(1.2 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}\). The chemical diffusivity of Sr is somewhat controversial. While the study of Sneeringer et al. (1984) indicates that this element has a faster diffusivity in clinopyroxene, compared with

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Table 2

Fixed and variable modeling parameters used in the one-dimensional model of Vasseur et al. (1991)

<table>
<thead>
<tr>
<th>Parameters common to all models</th>
<th>Cpx</th>
<th>Opx</th>
<th>Spl</th>
<th>Ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>porosity (m)</td>
<td>0.03</td>
<td>0.047</td>
<td>0.05</td>
<td>0.013</td>
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<tr>
<td>height of the column (m)</td>
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<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>melt velocity (cm s(^{-1}))</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>chemical diffusivity in melt (cm(^2) s(^{-1}))</td>
<td>(1 \times 10^{-8})</td>
<td>(1 \times 10^{-8})</td>
<td>(1 \times 10^{-8})</td>
<td>(1 \times 10^{-8})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral/melt partition coefficients</th>
<th>Cpx</th>
<th>Opx</th>
<th>Spl</th>
<th>Ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>0.37</td>
<td>0.047</td>
<td>0.05</td>
<td>0.013</td>
</tr>
<tr>
<td>Nd</td>
<td>0.3</td>
<td>0.012</td>
<td>0.01</td>
<td>0.00003</td>
</tr>
<tr>
<td>Sr</td>
<td>0.074</td>
<td>0.003</td>
<td>0.0002</td>
<td>0.00018</td>
</tr>
</tbody>
</table>

modal composition of the harzburgitic protolith

<table>
<thead>
<tr>
<th>Other parameters</th>
<th>Cpx</th>
<th>Opx</th>
<th>Spl</th>
<th>Ol</th>
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<tr>
<td>0.85</td>
<td>0.02</td>
<td>0.12</td>
<td>0.01</td>
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Element abundances in the infiltrated melt (ppm)

<table>
<thead>
<tr>
<th></th>
<th>models 4a/5a</th>
<th>models 4b/5b</th>
<th>models 4c/5c</th>
<th>models 4d/5d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf ppm</td>
<td>2.45</td>
<td>2.45</td>
<td>2.45</td>
<td>2.45</td>
</tr>
<tr>
<td>Nd ppm</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>743</td>
<td>743</td>
<td>743</td>
<td>743</td>
</tr>
</tbody>
</table>

Other parameters

<table>
<thead>
<tr>
<th></th>
<th>models 4a/5a</th>
<th>models 4b/5b</th>
<th>models 4c/5c</th>
<th>models 4d/5d</th>
</tr>
</thead>
<tbody>
<tr>
<td>grain size (mm)</td>
<td>3</td>
<td>0.1 to 3/1 to 5</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Chemical diffusivity in minerals (cm\(^2\) s\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>(1.2 \times 10^{-17}) to (3.4 \times 10^{-16})</th>
<th>(1.2 \times 10^{-17})</th>
<th>(1.2 \times 10^{-17})</th>
<th>(1.2 \times 10^{-17})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>(3.4 \times 10^{-17}) to (3.4 \times 10^{-16})</td>
<td>(3.4 \times 10^{-17})</td>
<td>(3.4 \times 10^{-17})</td>
<td>(3.4 \times 10^{-17})</td>
</tr>
<tr>
<td>Nd</td>
<td>(3.4 \times 10^{-18}) to (3.4 \times 10^{-16})</td>
<td>(3.4 \times 10^{-17})</td>
<td>(3.4 \times 10^{-17})</td>
<td>(3.4 \times 10^{-17})</td>
</tr>
<tr>
<td>Sr</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Element abundances in the infiltrated melt (ppm)

<table>
<thead>
<tr>
<th></th>
<th>models 4a/5a</th>
<th>models 4b/5b</th>
<th>models 4c/5c</th>
<th>models 4d/5d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf ppm</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Nd ppm</td>
<td>0.015</td>
<td>0.007</td>
<td>0.0022</td>
<td>0.015</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Ol = olivine; Opx = orthopyroxene; Cpx = clinopyroxene; Spl = spinel. CDIH is the critical distance of isotopic homogenization.
REE, the recent study of Von der Handt (2008) on orthopyroxene suggests that the diffusion of Sr is actually slower than that of REE, in both clin- and orthopyroxene. For this reason, we fixed the diffusivity of Sr identical to that of Nd. To assess the effect of chemical diffusivities variations, we run experiments involving variations of this parameter in the range 0.1 to 30 times the $d$ values. The observed range of pyroxenes grains sizes in Lherz varies from 1 to 4 mm (Le Roux et al., 2008), except in small-scale mylonitic zones (<1 mm). In the models, mineral grain size varies from 0.1 mm to 5 mm. This represents the average diameter of the grains, considered to be spherical. For simplicity, olivines and pyroxenes were considered to have the same size for modeling. The Hf, Nd and Sr contents in the protolith (based on the composition of the most depleted sample) are ~0.003, 0.015 and 1 ppm, respectively, and the Hf, Nd and Sr contents in the infiltrated melt (based on equilibrium with clinopyroxenes from distal, refertilized lherzolites) are ~2.45, 10.7 and 743 ppm, respectively. To evaluate the effect of the compositional contrast between melt and matrix, we run a series of experiments with a realistic range of daughter element variations in the harzburgites. $Hf_{matrix}/Hf_{matrix}$ ratios vary from 817 to 305, assuming constant $Hf_{melt}$ and $Nd_{matrix}/Nd_{matrix}$ and $Nd_{melt}/Nd_{matrix}$ ratios vary from 475 to 1420, assuming constant $Nd_{melt}$ and $Sr_{melt}/Sr_{matrix}$. The critical distance of isotopic homogenization along the column ranges between 0.1 and 10 m.

The parameters used in the percolation–reaction model of Vernières et al. (1997), such as porosity, isotopic ratios and elements concentrations, are the same as for the one-dimensional model. The melt-rock reaction was taken from Le Roux et al. (2007). It is a pyroxene-forming reaction at decreasing melt mass also involving some degree of olivine dissolution.

5.3. Results of the modeling

Representative results of the percolation–diffusion modeling are illustrated on Figs. 4 and 5. These figures show the isotopic covariations of Hf–Nd (Fig. 4) and Nd–Sr (Fig. 5) along the percolation column, from the composition of the harzburgite protolith (atop the column) to that of the melt (at base of the column). Both Hf–Nd and Nd–Sr covariations define curved trajectories that may be either convex upward, lying above the mixing lines, or convex downward, lying below the mixing lines. These variations imply significant inter-isotopic decoupling, notably for the Hf–Nd pair.

Drastic variations in the shape of the Hf–Nd isotopic covariation curves may indeed occur for relatively small variations of several critical parameters, namely: (1) element diffusivity in minerals (Fig. 4a), (2) average grain size of minerals (Fig. 4b), (3) compositional contrast between protolith and melt for the daughter elements Hf and Nd (Fig. 4c), and (4) critical distance of isotopic homogenization along the percolation column (Fig. 4d).

The convex-upward Hf–Nd isotopic covariation trend observed for high element diffusivities in minerals (Fig. 4a) and/or small grain

![Fig. 4.](image-url)
sizes (Fig. 4b) is consistent with the chromatography theory of trace-element reequilibration in porous flow systems (Navon and Stolper, 1987). The latter predicts that if the critical time of mineral/melt reequilibration by diffusion is short enough compared to the critical time of percolation (Vasseur et al., 1991) then Nd reequilibrates at lower melt/rock ratio than Hf due to its higher incompatibility degree, e.g. Kd_{Cpx/melt} = 0.30 for Nd compared with 0.37 for Hf (Blundy et al., 1998). This type of Hf–Nd decoupling is also in agreement with the classical assumption that Hf is more robust to mantle metasomatism than Nd (e.g. Bedini et al., 2004).

However, our experiments also show convex-downward Hf–Nd covariation trends that are opposite to the variation predicted by the chromatographic theory. At a given Hf_{melt}/Hf_{matrix} value, they are systematically observed in experiments involving relatively slow element diffusivities in minerals (Fig. 4a) and/or coarse grain sizes (Fig. 4b), i.e., when the critical time of solid–liquid equilibrium tends to be significant compared to the critical time of percolation (10^4 years in all our experiments). This type of Hf–Nd decoupling does not result from the difference in diffusivity between Hf and Nd as Hf diffuses at a slower rate than Nd. The convex-downward Hf–Nd trends reflect the persistence of solid–liquid chemical disequilibrium in significant parts of the percolation column – notably the uppermost part – where the

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Fig. 5. 143Nd/144Nd versus 87Sr/86Sr in clinopyroxene separates from Lherz harzburgites (open squares) and lherzolites (solid circles), compared with the mixing curve (dotted line) between a harzburgite protolith and a MORB-type melt, and with the results of the one-dimensional percolation–diffusion modeling (solid lines). The diagrams (a) to (d) illustrate the effects of varying parameters in the model: (a) diffusivities, d, of the elements in minerals; (b) the mineral grain size; (c) the Ndmelt/Nd_matrix ratio; (d) the critical distance of isotopic homogenization along the column.

Fig. 6. Results of percolation–reaction modeling (Vernières et al., 1997) for the Hf–Nd isotopes in the Lherz peridotites. Symbols are the same than in previous figures.
percolating melt and the matrix partly preserve their original compositions. In these conditions, the chromatographic fractionation process is overwhelmed by the compositional effect of Hf and Nd concentrations in the protolith and disequilibrium melt. This effect results from the dependence of the bulk (solid + melt) isotopic values calculated with the isotopic mixing equation at the scale of critical homogenization volumes on daughter element concentrations in minerals and melt.

For a given set of parameters consistent with the chromatography theory, the convex-upward Hf–Nd isotopic trends are observed in experiments involving relatively low concentration of Hf in melt relative to the matrix (Hfmelt/Hfmatrix < 443 for the experiments shown on Fig. 4c). However, a subtle increase of the Hf concentration in the melt relative to the matrix (Hfmelt/Hfmatrix = 443 to 817, i.e. Hf matrix = 0.008 to 0.003 on Fig. 4c) is sufficient to generate a change from convex-upward to convex-downward Hf–Nd isotopic covariation trends.

Finally, the amplitude of the transient Hf–Nd isotopic decoupling along the percolation column is negatively correlated with the efficiency of the isotopic homogenization process. Spatially limited homogenization (i.e., short critical distance of isotopic homogenization along the column) yields strongly convex Hf–Nd covariation curves, either upwards or downwards depending on the other model parameters (e.g., Fig. 4d). Conversely, in the limiting case where the critical distance of isotopic homogenization is of the same length as the percolating column, the result of the percolation–diffusion experiment is similar to that of a mixing between the protolith and the melt (Fig. 4d).

The Lherz data are best explained by a strongly convex-downward Hf–Nd trend (heavy line on Fig. 4). Within the range of parameters fixed from our petrographical observations (mineralogy and grain size), geochemical data (protolith and inferred melt composition) and published experimental works (partition and diffusion coefficients), this Hf–Nd variation implies that the critical size of the isotopic homogenization volumes was ≤ 1 m during the melt percolation event. The dispersion observed for a few samples may be accounted for by subtle variations of critical parameters such as the mineral grain size, or the Hf–Nd content in peridotite or percolating melt.

In contrast with the Hf–Nd isotopic covariations, the modeled Nd–Sr trends are generally hardly distinguishable from the mixing curves in the range of the parameter values constrained by the Lherz data and experimental works (Fig. 5). Within this range of parameters, most experiments yield moderately convex-downward trajectories consistent with the chromatographic theory which predicts that Sr reequilibrates at lower melt/rock ratio than Nd due to its higher incompatibility degree, e.g. Kd_{Cpx/melt} = 0.074 for Sr compared with 0.30 for Nd (Blundy et al., 1998). Noticeable exceptions are the experiments involving relatively high Nd_{melt}/Nd_{matrix} ratios (Fig. 5c). As previously noted by Ionov et al. (2002), the relative concentration of Nd and Sr in the protolith and disequilibrium melt are indeed critical parameters for the relative velocities of the Nd and Sr isotopic reequilibration fronts in a porous flow column. For Nd_{melt}/Nd_{matrix} values in the range defined by the theoretical melt in equilibrium with the Cpx of the distal ilherzolite and the distal harzburgites, the modeled Nd–Sr isotopic curves vary from moderately convex upward to moderately convex downward, on either side of the mixing curve. These variations encompass the whole range observed in the samples from the transition zone. In contrast with Hf–Nd, no inference on the size of the isotopic homogenization volumes can be drawn from the Nd–Sr covariance (Fig. 5d).

Representative results of the percolation–reaction modeling are illustrated on Fig. 6, showing the influence of the refertilization, meltrock reaction on isotopic reequilibration. In order to compare with the percolation–diffusion model, we first run experiments using the plate model without reaction. This yielded convex-upward Hf–Nd isotopic reequilibration trends consistent with the chromatography theory. Moreover, we show that melt-rock reactions at decreasing melt-mass enhance chromatographic effects by decreasing the porosity. This reflects the key role of porosity on chromatographic fractionation (Bodinier et al., 1990). Besides, isotopic signatures of the ilherzolites close to the contact are not consistent with isotopic signatures predicted by a mineralogical reaction, although they result from a refertilization reaction. Therefore, the percolation–reaction model strengthens previous results obtained with the one-dimensional percolation–diffusion model, where chemical diffusion is a required, critical parameter to explain isotopic reequilibration during melt percolation.

6. Conclusions

The isotopic heterogeneity observed in the transition zone between harzburgites and ilherzolites in the Lherz massif can be reproduced with a realistic range of physical parameters: a melt fraction of a few percent, a percolation rate of several cm y^{-1}, a distance of percolation from tens to several hundreds of meters associated with a volume of homogenization on the scale of the sample (some tens of cm). The Lherz example suggests that a large range of isotopic signatures may be generated at a melt percolation front, depending on chemical diffusion, isotopic homogenization and peridotite-melt compositions. We also show that mineralogical reactions at decreasing melt-mass enhance chromatographic effects by decreasing the porosity. The variations observed in the Lherz peridotites are more readily governed by diffusional peridotite-melt disequilibrium than by the chromatographic effect of melt transport and the refertilization reaction. The development of these signatures is a transient phenomenon associated with the passage of a percolation front which has been “frozen in” in the Lherz massif. Moreover, we observe that the microstructural characteristics (e.g. the grain size) of the percolated protolith strongly influence the resulting isotopic signature within the percolation front. Thus deformation and recrystallization of mantle rocks may induce local variations in isotopic signatures, as observed in the Ronda massif (Reisberg and Zindler, 1986) or in xenoliths from the French Massif Central (Downes and Dupuy, 1987). The world-wide association of LREE-enriched harzburgites with LREE-depleted ilherzolites, as observed in Lherz, suggests that the interaction of percolating melts with the lithospheric mantle is a widespread process. We observe that, under certain circumstances, these interactions can generate enriched, “intraplate-like” isotopic signatures in the transition zone between the two contrasting components. These results suggest that a part of isotopic signatures of mantle-related rocks could be generated by diffusional processes associated with melt transport.

Acknowledgements

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