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To cite this version:
Hugues Beunon, Nadine Mattielli, Luc S. Doucet, Bertrand N. Moine, Baptiste Debret. Mantle heterogeneity through Zn systematics in oceanic basalts: Evidence for a deep carbon cycling. Earth-Science Reviews, 2020, 205, pp.103174. 10.1016/j.earscirev.2020.103174. hal-02539535

HAL Id: hal-02539535
https://uca.hal.science/hal-02539535
Submitted on 12 Nov 2020

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Mantle heterogeneity through Zn systematics in oceanic basalts: Evidence for a deep carbon cycling

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ARTICLE INFO
Keywords: Zinc, Zinc isotopes, Radiogenic isotopes, Mantle heterogeneity, OIB, MORB, Deep carbon cycle

ABSTRACT
Subduction at convergent margins introduces a range of sedimentary and crustal materials into the mantle, providing the most dominant form of heterogeneity in the source of oceanic basalts. Yet, the relationship between geochemical variability and lithologic heterogeneities in the Earth’s mantle remains controversial. In this paper, we comprehensively review Zn, ⁶⁶Zn and Sr-Nd isotope systematics in near-primary basalts erupted at mid-ocean ridges (MORB) and ocean islands (OIB) to help constrain the nature and proportion of the carbon (C) bearing slab-derived component in their mantle sources. We show that Zn elemental and isotopic composition of oceanic basalts differs according to their tectonic settings, increasing from MORB (Zn = 62 ± 10 to 73 ± 11 ppm; ⁶⁶Zn = +0.24 ± 0.01 to +0.31 ± 0.02‰) to OIB (Zn = 74 ± 9 to 124 ± 7 ppm; ⁶⁶Zn = +0.21 ± 0.07 to +0.40 ± 0.04‰). Unlike MORB, the high Zn and ⁶⁶Zn recorded in OIB cannot be explained by partial melting of a fertile peridotite mantle source only. Importantly, global correlations between Zn content and Sr-Nd isotopes in oceanic basalts suggest that the Zn enrichment in OIB is inherited from a recycled component in their mantle source rather than melting processes. We demonstrate that involvement of neither typical MORB-like oceanic crust nor subducted sediments can achieve the whole range of Zn composition in OIB. Instead, addition of ≤6% C-bearing oceanic crust to a fertile peridotite mantle fully resolves the Zn heterogeneity of OIB, both in terms of magnitude of Zn enrichment and global trends with Sr-Nd isotopes. Such scenario is corroborated by the elevated ⁶⁶Zn of OIB relative to MORB and mantle peridotites, reflecting the contribution of isotopically heavy C-bearing phases (⁶⁶Zn = +0.91 ± 0.24‰) to the mantle source (⁶⁶Zn = +0.16 ± 0.06‰). Our study thus emphasizes the use of Zn and ⁶⁶Zn systematics to track the nature and origin of mantle carbon, highlighting the role of subduction in the deep carbon cycle. Finally, the positive correlation between Zn content and temperature of magma generation of oceanic basalts suggests that hotter mantle plumes are more likely to carry a higher proportion of dense C-bearing eclogite. Zinc systematics therefore may provide evidence that the presence of heterogeneous domains in the source of OIB is, at least partly, linked to plume thermal buoyancy, bringing new insights into mantle dynamics.

1. Introduction
Geophysical and geochemical heterogeneities have long been recognized within the Earth's mantle. The mantle was initially inferred from trace elements, and long-lived radiogenic isotopes (e.g., Sr, Nd, Hf, Pb) variations in basalts erupted at mid-ocean ridges (MORB) and ocean islands (OIB). Their geochemical signature reflects the compositional heterogeneity of the mantle and its evolution through time (e.g., Hofmann, 1997; Willbold and Stracke, 2006; Zindler and Hart, 1986). It is widely accepted that these heterogeneities involve ancient and deeply subducted sediments, oceanic crust and underlying lithosphere introduced in the mantle at convergent margins. Eclogites (i.e., olivine-free, clinopyroxene- and garnet-bearing rocks) derived from the recycled oceanic crust and sediments are then entrained and stirred by convection, providing one of the most dominant form of heterogeneity in the mantle source of oceanic basalts. However, the specific nature and proportion of the slab-derived eclogitic component in the mantle is still a matter of speculation (see Anderson, 2006 and references therein). Subducted eclogites may derive from a typical MORB oceanic crust (e.g., silica-excess and volatile-free, hereafter referred as MORB-

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https://doi.org/10.1016/j.earscirev.2020.103174
Received 11 November 2019; Received in revised form 18 March 2020; Accepted 27 March 2020
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Please cite this article as: Hugues Beunon, et al., Earth-Science Reviews, https://doi.org/10.1016/j.earscirev.2020.103174
eclogite) that can be carbonitized during seafloor hydrothermal alteration (e.g., silica-deficient and carbon-bearing, hereafter referred as C-bearing eclogites; Nakamura and Kato, 2004; Kitajima et al., 2001). However, little is known about the relationship between geochemical variability and lithologic heterogeneities in the Earth’s mantle. While incompatible trace element variations highlight distinct geochemical imprints between MORB and OIB, they do not provide information about the exact nature and extent of mineralogical variability in the source regions of oceanic basalts. Yet, characterization of such lithologic heterogeneities is of prime importance for constraining the physical properties of the mantle (e.g., thermal state, viscosity and density), understanding the dynamics of the Earth (e.g., differentiation and melting processes) and bridging geochemical and geophysical observations. Several studies have tried to tackle the question of mineralogical heterogeneities in the mantle focusing on major oxide and siderophile element systematics in oceanic basalts (Le Roux et al., 2010, 2011, 2015). In this paper, we present a comprehensive review of Zn, $^{66}$Zn and Sr-Nd isotopic composition and Sr-Nd isotopic composition in oceanic basalts worldwide and reassess the use of Zn as a tracer of eclogite-derived melts. We show that Zn abundances correlate with Sr-Nd isotopes on a single ridge and ocean island group basis. This result, together with the extreme Zn enrichment in OIB cannot be readily explained by melting and mixing of fertile peridotite and MORB-eclogite as previously suggested. Instead, our results point towards the involvement of Zn-rich C-bearing eclogites. On the basis of a compilation of Zn isotopic data from previous studies and new unpublished data from the Crozet archipelago, we argue that such scenario is corroborated by the heavy $^{66}$Zn of OIB relative to MORB and mantle peridotites. Thus, Zn systematics may provide a valuable tool to fingerprint recycling of C-bearing subducted materials and deep carbon cycling in the Earth’s mantle. 2. Materials and methods 2.1. Data selection and filtering We compiled zinc abundances, major oxide concentrations and radiogenic Sr-Nd isotopic composition of oceanic basalts from the GEOROC (http://georoc.mpch-mainz.gwdg.de/georoc) and PetDB (www.earthcem.org/petdb) databases. Basalts with LOI > 3 wt% and sum of oxides < 97 wt% or > 102 wt% calculated on a dry basis were systematically excluded from the filtered database. Major element contents of the remaining samples were then normalized to 100 wt% on a dry-weight basis with all Fe reported as FeOT. Since we aim to picture global-scale variations in oceanic basalts (i.e., MORB and OIB), average near-primary compositions were calculated on a single ridge and ocean island group basis (i.e., MORB and OIB). Table 1 Average Zn concentration (ppm), Zn/Fe ratio, MgO (wt%), FeO$^+$ (wt%) and Sr-Nd isotopic composition in peridotites and near-primary basalts from selected locations.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Zn (ppm)</th>
<th>Zn/Fe (x10$^3$)</th>
<th>MgO (wt%)</th>
<th>FeO T (wt%)</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>$^{143}$Nd/$^{144}$Nd</th>
<th>T_Lee (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peridotites</td>
<td>52 ± 9</td>
<td>8.2 ± 1.3</td>
<td>42.8 ± 2.7</td>
<td>8.1 ± 0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lherzolites</td>
<td>54 ± 8</td>
<td>8.5 ± 1.2</td>
<td>41.6 ± 2.1</td>
<td>8.2 ± 0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Harzburgites</td>
<td>48 ± 8</td>
<td>7.8 ± 1.3</td>
<td>45.5 ± 1.6</td>
<td>8.0 ± 0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MORB</td>
<td>68 ± 12</td>
<td>9.6 ± 1.5</td>
<td>9.7 ± 1.1</td>
<td>9.0 ± 1.0</td>
<td>0.70284 ± 31</td>
<td>0.51308 ± 10</td>
<td>-</td>
</tr>
<tr>
<td>EPR</td>
<td>62 ± 10</td>
<td>9.0 ± 1.6</td>
<td>9.9 ± 1.3</td>
<td>8.6 ± 1.3</td>
<td>0.70254 ± 9</td>
<td>0.51314 ± 5</td>
<td>1371 ± 41</td>
</tr>
<tr>
<td>Gakkel</td>
<td>64 ± 2</td>
<td>9.2 ± 0.6</td>
<td>9.1 ± 0.1</td>
<td>9.0 ± 0.6</td>
<td>0.70290 ± 6</td>
<td>0.51312 ± 8</td>
<td>1387 ± 42</td>
</tr>
<tr>
<td>MAR</td>
<td>70 ± 12</td>
<td>9.8 ± 1.4</td>
<td>9.8 ± 1.2</td>
<td>9.2 ± 0.9</td>
<td>0.70291 ± 28</td>
<td>0.51307 ± 10</td>
<td>1412 ± 42</td>
</tr>
<tr>
<td>SEIR</td>
<td>70 ± 13</td>
<td>9.4 ± 1.2</td>
<td>9.4 ± 0.3</td>
<td>9.6 ± 1.4</td>
<td>0.70305 ± 26</td>
<td>0.51307 ± 12</td>
<td>-</td>
</tr>
<tr>
<td>SWIR</td>
<td>73 ± 11</td>
<td>10.2 ± 1.0</td>
<td>9.4 ± 0.3</td>
<td>9.2 ± 1.0</td>
<td>0.70322 ± 38</td>
<td>0.51299 ± 7</td>
<td>-</td>
</tr>
<tr>
<td>MORB-related OIB</td>
<td>79 ± 13</td>
<td>10.1 ± 1.0</td>
<td>11.0 ± 1.4</td>
<td>10.1 ± 0.9</td>
<td>0.70357 ± 68</td>
<td>0.51296 ± 14</td>
<td>-</td>
</tr>
<tr>
<td>Iceland</td>
<td>74 ± 9</td>
<td>9.7 ± 0.7</td>
<td>11.2 ± 1.3</td>
<td>9.7 ± 0.8</td>
<td>0.70317 ± 16</td>
<td>0.51305 ± 6</td>
<td>1431 ± 43</td>
</tr>
<tr>
<td>Galapagos</td>
<td>84 ± 15</td>
<td>10.5 ± 1.3</td>
<td>10.4 ± 1.4</td>
<td>10.2 ± 0.9</td>
<td>0.70310 ± 30</td>
<td>0.51302 ± 6</td>
<td>1462 ± 44</td>
</tr>
<tr>
<td>Azores</td>
<td>86 ± 10</td>
<td>10.7 ± 1.2</td>
<td>10.9 ± 1.7</td>
<td>10.4 ± 0.7</td>
<td>0.70367 ± 32</td>
<td>0.51290 ± 5</td>
<td>1477 ± 44</td>
</tr>
<tr>
<td>Kerguelen</td>
<td>94 ± 8</td>
<td>10.5 ± 0.8</td>
<td>10.7 ± 1.2</td>
<td>11.5 ± 0.5</td>
<td>0.70484 ± 37</td>
<td>0.51270 ± 9</td>
<td>1514 ± 45</td>
</tr>
<tr>
<td>OIB</td>
<td>108 ± 15</td>
<td>11.6 ± 1.7</td>
<td>11.3 ± 1.7</td>
<td>12.0 ± 0.9</td>
<td>0.70414 ± 98</td>
<td>0.51284 ± 12</td>
<td>-</td>
</tr>
<tr>
<td>St Helena</td>
<td>93 ± 7</td>
<td>9.7 ± 0.5</td>
<td>11.8 ± 1.8</td>
<td>12.3 ± 0.6</td>
<td>0.70288 ± 5</td>
<td>0.51287 ± 3</td>
<td>1587 ± 48</td>
</tr>
<tr>
<td>Mascarene</td>
<td>102 ± 13</td>
<td>10.7 ± 1.5</td>
<td>11.1 ± 1.5</td>
<td>12.3 ± 1.0</td>
<td>0.70398 ± 20</td>
<td>0.51288 ± 5</td>
<td>1565 ± 47</td>
</tr>
<tr>
<td>Hawaii</td>
<td>103 ± 13</td>
<td>11.3 ± 1.6</td>
<td>10.8 ± 1.6</td>
<td>11.7 ± 0.8</td>
<td>0.70362 ± 14</td>
<td>0.51293 ± 8</td>
<td>1521 ± 46</td>
</tr>
<tr>
<td>Pitcairn</td>
<td>106 ± 13</td>
<td>12.0 ± 1.8</td>
<td>12.2 ± 1.8</td>
<td>11.5 ± 0.6</td>
<td>0.70468 ± 27</td>
<td>0.51257 ± 7</td>
<td>1522 ± 46</td>
</tr>
<tr>
<td>Canary</td>
<td>108 ± 16</td>
<td>11.3 ± 1.5</td>
<td>11.2 ± 1.6</td>
<td>12.3 ± 1.0</td>
<td>0.70320 ± 17</td>
<td>0.51294 ± 3</td>
<td>1577 ± 47</td>
</tr>
<tr>
<td>Cape Verde</td>
<td>110 ± 8</td>
<td>12.7 ± 1.0</td>
<td>12.1 ± 1.7</td>
<td>11.1 ± 0.5</td>
<td>0.70341 ± 6</td>
<td>0.51277 ± 3</td>
<td>1540 ± 46</td>
</tr>
<tr>
<td>Comoros</td>
<td>110 ± 14</td>
<td>11.5 ± 1.4</td>
<td>11.1 ± 0.4</td>
<td>12.3 ± 0.2</td>
<td>0.70348 ± 15</td>
<td>0.51279 ± 6</td>
<td>1590 ± 48</td>
</tr>
<tr>
<td>Cook-Austral</td>
<td>114 ± 15</td>
<td>12.1 ± 1.5</td>
<td>12.4 ± 1.4</td>
<td>12.3 ± 0.7</td>
<td>0.70310 ± 40</td>
<td>0.51290 ± 5</td>
<td>1594 ± 48</td>
</tr>
<tr>
<td>Marquesas</td>
<td>117 ± 6</td>
<td>12.7 ± 0.6</td>
<td>11.5 ± 2.0</td>
<td>11.8 ± 0.7</td>
<td>0.70412 ± 56</td>
<td>0.51284 ± 20</td>
<td>1526 ± 46</td>
</tr>
<tr>
<td>Society</td>
<td>124 ± 7</td>
<td>13.3 ± 0.7</td>
<td>12.2 ± 1.7</td>
<td>12.0 ± 0.9</td>
<td>0.70502 ± 61</td>
<td>0.51274 ± 6</td>
<td>1566 ± 47</td>
</tr>
<tr>
<td>Samoa</td>
<td>124 ± 12</td>
<td>13.1 ± 1.1</td>
<td>11.8 ± 1.4</td>
<td>12.2 ± 1.1</td>
<td>0.70562 ± 69</td>
<td>0.51273 ± 5</td>
<td>1572 ± 47</td>
</tr>
</tbody>
</table>
(n = 694) from Iceland, Hawaii, the Azores, Kerguelen, Galapagos, Samoa, Society, Marquesas, Mascarene, Cook-Austral, Comoros, Cape Verde, Canary, Pitcairn and St Helena Islands. We also compiled Zn data of fertile lherzolites (n = 269) and residual harzburgites (n = 124) from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc, petrological names as given in the GEOROC database). Because Zn elemental composition may have been modified during secondary processes such as serpentinization (Debret et al., 2018b) peridotites with loss on ignition (LOI) > 3 wt% were discarded from our compilation. Average composition of peridotites and oceanic basalts from distinct ridges and ocean islands are summarized in Table 1 (see Appendix 1 for the whole filtered dataset and references).

Published Zn isotopic compositions of oceanic basalts are much more sparse in comparison to Zn elemental data precluding a detailed examination of δ66Zn variations on a single ridge or ocean island basis. Here we compiled a dataset of 47 δ66Zn values including MORB (n = 13) from the MAR, SEIR, SWIR, Galapagos ridge and Carbros ridge and OIB (n = 34) from Hawaii, Iceland, the Canary and Reunion islands (see Appendix 2 for the whole dataset and references). Given the limited δ66Zn fractionation during fractional crystallization (see Section 3.1) and the limited availability of data, we consider a slightly expanded range of MgO for near-primary basalts (6 wt% < MgO < 16 wt%) totaling 24 δ66Zn values for undifferentiated oceanic basalts worldwide (Table 2).

2.2. Acquisition of new Zn and δ66Zn data from Crozet Archipelago

New δ66Zn MC-ICP-MS data and associated Zn concentrations determined by ICP-MS in 11 basaltic samples from the Penguins island (Crozet Archipelago) were also determined to expand the pre-existing database (Table 2, see Appendix 3 for detailed results). Petrographic and geochemical characterization of the selected samples including major and other trace elements data are available in Breton et al. (2013). Measurements were carried out on bulk-rock powders at the Laboratoire G-Time, Université Libre de Bruxelles (ULB). About 50 mg of powdered samples were dissolved using a 3:2 mix of concentrated HF and HNO3 in square bodied Teflon vials (© Savillex) at 130 °C on a hotplate. Samples were then dried down and further attacked with a 1:1 mix of concentrated HCl and HNO3. All reagents were distilled in subboiling Teflon two-bottle stills at the ULB. After total digestion samples were split into two aliquots and Zn concentrations were analyzed in 5% HNO3 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, © Agilent 7700×) giving a mean agreement with previous studies (+0.29 ± 0.04‰ (2SD, n = 9) in good agreement with previous studies (+0.29 ± 0.04‰, http://georoc.mpch.mainz.gwdg.de). External geostandards BHVO-2 and BCR-2 (basalts, USGS) were processed through chemistry and analyzed alongside samples. Total duplicates of sample OVPG-13 and OVPG-38 yielded standard deviation of ± 0.01 and ± 0.03 (2SD, respectively). Zn isotopic compositions are reported with the delta value in per mille notation (‰) using the conventional conversion equation from Hoefs (2018). Re-ference materials BHVO-2 and BCR-2 (basalts, USGS) were processed through chemistry and analyzed alongside samples. Total duplicates of sample OVPG-13 and OVPG-38 yielded standard deviation of ± 0.01 and ± 0.03 (2SD, respectively).

2.3. Two-component melting-mixing model

The composition of oceanic basalts was modeled considering mixing...
of partial melts from a fertile peridotite (spinel- or garnet-bearing) and recycled components (i.e., sediment, MORB-eclogite or C-bearing eclogite). The trace element composition of the residue (C$_{\text{residue}}$) and melt (C$_{\text{melt}}$) at a given degree of melt extraction (F) is calculated using the accumulated fractional modal melting equations from Shaw (1970):

\[ C_{\text{residue}} = C_0 * (1 - F)^{1/D_0 - 1} \]
\[ C_{\text{melt}} = C_0 * (1 - (1 - F)^{1/D_0})/F \]

where $C_0$ and $D_0$ are the concentration and bulk partition coefficient of the trace element in the source, respectively. The bulk partition coefficient $D_0$ is function of the modal proportions ($X_i$) and individual mineral-melt partition coefficients ($D_i^{\text{mineral-melt}}$ or $D_i$) of the rock-forming minerals in the source ($D_0 = \Sigma D_i * X_i$). To model the range of stable isotope fractionation induced by partial melting in the residue ($\delta_{\text{residue}}$) and melt ($\delta_{\text{melt}}$), we use the Rayleigh distillation equations from Hoefs (2018):

\[ \delta_{\text{residue}} = (1000 + \delta_0) * f^{(a-1)} - 1000 \]
\[ \delta_{\text{melt}} = (1000 + \delta_0) * (1 - f^a)/(1 - f) - 1000 \]

where $\delta_0$ is the stable isotope composition of the source, $f$ is the remaining fraction of the element in the residue ($f = 1 - F * C_{\text{residue}}/C_0$) and $a$ is the isotopic fractionation factor between solid and melt. The isotopic fractionation factor $a$ reflects the $\delta$ difference between the melt and the residue ($\delta_{\text{melt}} - \delta_{\text{residue}}$ in $\delta$ (a $\approx 1000$), which is function of the modal proportions ($X_i$) and individual mineral-melt partitioning of the rock-forming minerals in the source ($\delta_{\text{melt}} - \delta_{\text{residue}} = \Sigma D_i^{\text{mineral-melt}} * X_i$). Aggregate fractional melts from a fertile peridotite and recycled material are then mixed and the elemental ($C_{\text{mix}}$) and isotopic ($\delta_{\text{mix}}$) composition of the hybrid melt are given by the equations from DePaolo (1981):

\[ C_{\text{mix}} = X_A * C_A + X_B * C_B \]
\[ \delta_{\text{mix}} = \delta_A * X_A + \delta_B * X_B \]

where $X_A, X_B, C_A, C_B, \delta_A$ and $\delta_B$ are the proportion, concentration and isotope composition of melts A and B, respectively. All modeling parameters are given in Table 3. Detailed results are provided in Appendix 4 and the composition of mixed melts from a fertile peridotite and sediments (brown curve and light brown field), MORB-eclogite (yellow curve) or C-bearing eclogite (black curve) sources are shown in Fig. 3–5. The C-bearing eclogite source is less constrained than sediments and MORB-eclogite. Hence, we also performed a melting-mixing Monte Carlo simulation accounting for the small but noteworthy compositional variability of C-bearing eclogites and the uncertainty on their estimated $\delta^{66}$Zn (see Appendix 4 and blue dots overlay in Fig. 3–5). Our melting-mixing model is a simplification of natural systems designed to evaluate the potential of Zn and Zn isotopes to trace recycled C-bearing material in the mantle source of oceanic basalts. Re-melting of metasomatized peridotites and hybrid pyroxenites formed by reaction between eclogite-derived melts and ambient peridotite has also been proposed to explain the compositional heterogeneity of oceanic basalts (Herzberg, 2006; Sobolev et al., 2005, 2007). However, hybridization processes and the resulting mineralogy of the refertilized mantle remain unconstrained at that time (e.g., Mallik and Dasgupta, 2012). Our study does not exclude such melt-rock reactions but a more elaborate investigation of their role on Zn heterogeneity in oceanic basalts would be highly speculative, limiting their consideration in the present model.

### 3. Discussion

#### 3.1. Zinc behavior during igneous differentiation and subduction processes

A primary implicit assumption for the use of Zn and Zn isotopes as tracers of recycled material and deep carbon cycling in the mantle is that they suffer little or no fractionation during igneous and subduction processes. The composition of oceanic basalts, however, may vary considerably during magmatic differentiation and no longer truly reflect the signature of their mantle sources (e.g., Teng et al., 2008; Williams et al., 2009 for Fe; Savage et al., 2011 for Si). Fractionation of fluid-mobile elements and their stable isotopes can also be significant during prograde metamorphism and dehydration accompanying subduction (e.g., Zack et al., 2003 for Li; Debret et al., 2016, 2018a for Fe). Therefore, the magnitude of Zn and $\delta^{66}$Zn fractionation induced by (1) partial melting, (2) subsequent fractional crystallization and (3) subduction zone metamorphism must first be addressed.

#### 3.1.1. Partial melting

In contrast to REE and other highly incompatible trace elements, most FRTEs have a $D_{\text{mineral-melt}}$ close to unity in olivine (Ol) and orthopyroxene (Opx), the two most abundant minerals in peridotites (Table 1, Le Roux et al., 2011; Davis et al., 2013; Mallmann and O’Neill, 2009). As such, FRTEs have a bulk partition coefficient $D_{\text{source-melt}}$ of 1 and remain relatively unfractionated during partial melting of a peridotite source (C$_{\text{residue}}$ ~ C$_{\text{melt}}$ ~ C$_{\text{source}}$). Interestingly, some FRTEs exhibit more variable $D_{\text{mineral-melt}}$ in clinopyroxene (Cpx) and/or garnet (Gt, Le Roux et al., 2011). Therefore, eclogite and peridotite derived melts will have distinct FRTE signatures, which has been used to trace mineralogical heterogeneities in the mantle (see Yang et al., 2016 and references therein). However, element partitioning is not solely controlled by the modal mineralogy of the source rock but varies by orders of magnitude with changes in temperature (T), pressure (P), melt composition and/or redox conditions (Blundy and Wood, 2003; Wood and Blundy, 2002; O’Neill and Egins, 2002). Among the FRTEs, Zn is a lithophile element with a single valence state (Zn$^{2+}$) at upper mantle conditions. Sulphides are known to be ubiquitous accessory phases in the silicate mantle, and Zn may also behave as a chalcophile element (average $D_{\text{Zn-sulphide-silicate}}$ ~ 3.5 ± 0.05, Pattan et al., 2013; Wood and Kiseeva, 2015). Yet, contribution of sulphides to the bulk $D_{\text{Zn}}$ during mantle melting is negligible (~0.002% assuming a weight fraction of 5.10$^{-4}$% of sulphides, Pattan et al., 2013). Because the Zn/Fe ratio remains relatively unaffected by metasomatic processes and its partitioning appears to be even more P-T independent, Le Roux et al. (2015) further advocate for the use of this geochemical proxy rather than simply Zn systematics. Zn/Fe is also redox-sensitive (i.e., Fe$^{3+}$ is more incompatible than Fe$^{2+}$ and Zn$^{2+}$, Lee et al., 2010), but any oxygen fugacity ($f_{\text{O}_2}$) dependency can be ruled out for MORB and OIB given that they have similar oxidation state (Frost and McCammon, 2008). As a result, Zn/Fe ratios in oceanic basalts are likely to carry the signature of the mineralogy of their sources (i.e. peridotite vs eclogite) irrespective of the presence of accessory sulphides, $f_{\text{O}_2}$ and P-T conditions during the onset of melting and percolation of hydrous fluids and melts (Le Roux et al., 2010, 2011, 2015).

In terms of Zn stable isotopes, equilibrium fractionation decreases proportionally to 1/T$^2$ (Urey, 1947; Schauble, 2004). Consequently, and considering that Zn is barely fractionated during mantle melting (i.e., C$_{\text{residue}}$ ~ C$_{\text{melt}}$ ~ C$_{\text{source}}$), Sossi et al. (2018) argued that $\delta^{66}$Zn enrichment in primary basaltic melts should not exceed +0.08% relative to their sources. Mass balance implies minimal Zn isotope variations in the residual peridotite counterpart (up to 0.0015% after 30% partial melting, Sossi et al., 2018). This result is in good agreement with the tight range of $\delta^{66}$Zn in unaltered mantle peridotites (average $\delta^{66}$Zn = +0.18 ± 0.06‰, Sossi et al., 2018; Doucet et al., 2016; Wang et al., 2017; Huang et al., 2018b). Incorporation of any isotopically offset component in the mantle (i.e., $\Delta^{66}$Zn$_{\text{exotic component}}$ ~ mantle > > 0.08‰) is thus expected to generate larger $\delta^{66}$Zn anomalies in oceanic basalts than melting processes. In turn, $\delta^{66}$Zn variations in MORB and OIB -if any- may be used to track the presence of isotopically light or heavy recycled material in their sources.

#### 3.1.2. Fractional crystallization

Olivine is the primary host of Zn among silicates crystallising from
basaltic magmas (Doe, 1995; Le Roux et al., 2010). Given that $D_{\text{Zn}}^{\text{ol-melt}}$ and $D_{\text{Zn}}^{\text{pl-melt}}$ are both close to one, olivine crystallization or accumulation has minimal effect on the Zn and Zn/Fe composition of basaltic melts. However, Zn is more incompatible in other silicates, especially in clinopyroxene ($D_{\text{Zn}}^{\text{pyx-melt}}$ = 0.3–0.7, Le Roux et al., 2015) and plagioclase ($D_{\text{Zn}}^{\text{pl-melt}}$ = 0.2, Ewart and Griffin, 1994). Because these two phases appear on the cotectic at ~8 wt% MgO (Jenner and O'Neill, 2012), the Zn content and Zn/Fe ratio of basaltic melts are expected to increase drastically in more differentiated magmas. This assumption is readily assessed in the example of Icelandic basalts provided in Supplementary Fig. 1a, b. Samples display a clear trend of increasing Zn and Zn/Fe with falling MgO, from ~75 ppm of Zn and Zn/Fe of ~9.5 × 10$^4$ at MgO ~10–15 wt% to ~175 ppm of Zn and Zn/Fe of ~15 × 10$^4$ at MgO ~5 wt%. These observations highlight the importance of our filtering scheme to study the most primary melts (9 wt% < MgO < 16 wt%) for tracing mantle heterogeneities.

Based on suites of cogenetic samples, Chen et al. (2013) showed that fractional crystallization of isotopically light olivine (66Zn up to −0.30 ± 0.02‰, McCoy-West et al., 2018) ± Fe-Ti oxides might induce a Zn isotopic shift up to ~0.10‰ with increasing degree of differentiation. Namely, 66Zn in samples from Kiluaea Iki lava lake (Hawaii) range from +0.29 ± 0.04‰ in near-primary basalts (12.0 wt % MgO) to +0.36 ± 0.04‰ in more compositionally-evolved melts (2.4 wt% MgO, Chen et al., 2013). Conversely, 66Zn values as low as +0.18 ± 0.00‰ and +0.04 ± 0.01‰ in high-MgO picrites and cumulate komatites have been attributed to accumulation of isotopically light olivines (McCoy-West et al., 2018; Sossi et al., 2018). For basaltic samples with 6 wt% < MgO < 16 wt%, however, there is no correlation between Zn isotope composition and degree of differentiation within analytical uncertainty. The data reported for basanites and picrites from the Crozet archipelago in this study further confirm these observations (Supplementary Fig. 2). Hence, 66Zn systematics in near-primary melts can be used to trace recycled material in their mantle sources.

### 3.1.3. Subduction zone metamorphism

Zinc isotopes can be significantly fractionated during fluid-rock interactions (Debret et al., 2018b). Pons et al. (2016) reported a progressive decrease of 66Zn in subducted serpentinites with increasing metamorphic grade and degree of dehydration, from greenschist (66Zn = +0.32 ± 0.08‰) to eclogite (66Zn = +0.16 ± 0.06‰) P-T facies conditions. Similarly, Debret et al. (2018a) showed the existence of anomalously low 66Zn in decarbonated serpentinites (66Zn down to ~ −0.56 ± 0.02‰) relative to C-bearing serpentinites (66Zn = +0.21–0.05‰) from blueschist terrains. Both observations clearly point towards the release of isotopically heavy-66Zn, S- and C-bearing dehydration fluids during serpentine breakdown and decarbonation of the serpentinitized slab mantle. However, it remains an active research topic to determine (1) whether Zn-bearing fluids are released at discrete metasomatic interfaces or broader portions of the slab serpentinites; and (2) whether these fluids are sufficiently concentrated in Zn to deeply influence the signature of the dehydrated slab (and/or that of the sub-arc mantle).

In contrast with serpentinites, no systematic Zn isotope fractionation has been reported in the mafic lithologies of the subducted slab, irrespective of their metamorphic facies (i.e., from greenschist to eclogite P-T conditions) and/or indicators of fluid-rock interaction (Inglis et al., 2017; Xu and Liu, 2018). Rather, the 66Zn signature of basaltic eclogites (66Zn = +0.27 ± 0.08‰, Inglis et al., 2017) overlaps with their inferred MORB (66ZnMORB = +0.27 ± 0.05‰, Huang et al., 2018a; Wang et al., 2017) or Altered Oceanic Crust (66ZnAOC = +0.27 ± 0.01‰, Huang et al., 2016) protoliths.
Continental margin sediments and subducted metasediments also display similar, although more variable, range of $\delta^{66}$Zn composition with an average of $+0.07 \pm 0.11$‰ and $+0.06 \pm 0.19$‰, respectively (Little et al., 2016; Inglis et al., 2017). Collectively, this suggests that relatively small amounts of Zn are mobilized from the subducted mafic oceanic crust and associated metasediments in S- or C-bearing dehydration fluids surging subduction zones. Most importantly, crustal and meta-sedimentary materials may retain, at least partly, their abyssal Zn isotope signature during subduction. Given the strong affinity of isotopically heavy Zn for either reduced or oxidized C-bearing material (Ducher et al., 2016; Fujii et al., 2011; Black et al., 2011), it seems therefore reasonable to consider the recycling of a C-bearing eclogite crust with a heavy $\delta^{66}$Zn signature in our models.

3.2. Zinc inventory of oceanic basalts

Zinc content of oceanic basalts originating from ridges, plumes or plume-ridge interaction differ according to their tectonic settings (Table 1 and Fig. 1a–c). MORB display the lowest Zn contents ($68 \pm 12$ ppm, all MORB average) and Zn/Fe ratios ($9.6 \pm 1.5 \times 10^4$), only slightly higher than average mantle peridotites ($Zn = 52 \pm 9$ ppm; $Zn/Fe = 8.2 \pm 1.3 \times 10^4$). Using recommended mineral-melt partition coefficients (Le Roux et al., 2015) and mineralogy estimates of the primitive mantle (Table 3, Wasylenki, 2003; Walter, 1998), we find a bulk $D_{Zn\ peridotite-melt}$ of 0.68–0.90 and $D_{Zn\ peridotite-melt}$ of 0.83–0.99 for melting of a spinel- or garnet-bearing peridotite. As the melting degree ($F$) tends towards zero, the maximum
Zn concentration and Zn/Fe ratio induced by melting of a primitive mantle source (ZnPM = 53.5 ppm and Zn/FePM = 8.5 \times 10^4, Palme and O'Neill, 2007) should not exceed 78 ppm and 9.8 \times 10^4, respectively (Eq. (2)). This result is perfectly in line with the full range of Zn (62 \pm 10 to 73 \pm 11 ppm) and Zn/Fe (9.0 \pm 1.6 to 10.2 \pm 1.0 \times 10^4) observed in basalts erupted at mid-ocean ridges. MORB also have homogeneous and slightly heavier $\delta^{66}$Zn values (+0.24 \pm 0.01 to +0.31 \pm 0.02‰) relative to average unmetasomatized peridotites (+0.18 \pm 0.06‰). Based on individual $\Delta_{\text{mineral-melt}}$ (Table 3, Sossi et al., 2018; McCoy-West et al., 2018) and primitive mantle estimates ($\delta^{66}$ZnPM = +0.16 \pm 0.06‰, Sossi et al., 2018), a maximum $\delta^{66}$Zn of +0.23‰ is modeled in the peridotite melt (Eq. (4)). This result is in reasonably good agreement with the average $\delta^{66}$Zn of all MORB (+0.28 \pm 0.04‰).

In contrast, OIB exhibit more variability than MORB and mantle peridotites (Table 1 and Fig. 1a–c). Zn, Zn/Fe and $\delta^{66}$Zn increase from OIB suites near or on active ridges (Zn = 74 \pm 9 to 94 \pm 8 ppm, Zn/Fe = 9.7 \pm 0.7 to 10.5 \pm 0.8 \times 10^4, $\delta^{66}$Zn = +0.21 \pm 0.07‰) to OIB far from ridges (Zn = 93 \pm 7 to 124 \pm 7 ppm, Zn/Fe = 9.7 \pm 0.5 to 13.3 \pm 0.7 \times 10^4, $\delta^{66}$Zn = +0.25 \pm 0.04 to +0.40 \pm 0.04‰). This observation reflects the well-known plume-ridge interactions of Schilling et al. (1983) nicely illustrated in the example of MORB from the SWIR provided in Fig. 2. In any case, both Zn elemental and isotopic compositions of OIB are irreconcilable with partial melting of a primitive mantle source only, suggesting the participation of an additional component.

Another striking feature is the global correlation between Zn abundance and Sr-Nd radiogenic isotopes in MORB, MORB-related OIB and OIB far from ridges (Fig. 3a, b). Such complementary results are not surprising given the global correlation between $^{87}/^{86}$Sr and $^{143}/^{144}$Nd in oceanic basalts (e.g., Hofmann, 1997 and references therein). This crucial observation, however, clearly points towards a Zn enrichment in OIB inherited from the source rather than melting processes. Unfortunately, the relationship between $\delta^{66}$Zn and Sr-Nd isotopes in basalts from our compilation cannot be investigated due to the lack of available data and calls for further investigations. All of these observations indicate that the putative recycled component(s) in the source of OIB must display (1) high Zn content and Zn/Fe ratio, (2)...
isotopically heavy $\delta^{66}Zn$ signature and (3) relatively radiogenic $^{87/86}Sr$ and un radiogenic $^{143/144}Nd$ signatures relative to the terrestrial mantle. In the following sections, we investigate the effect of addition of recycled subducted material (i.e., sediment, MORB-eclogite and C-bearing eclogite) on the Zn composition of oceanic basalt.

### 3.3. MORB-type ocean crust recycling

Based on the lower $D_{Zn/Fe}^{\text{mineral-melt}}$ of clinopyroxene and garnet relative to olivine and orthopyroxene (Table 3, Le Roux et al., 2015) argued that the high Zn/Fe recorded in OIB derive from melting of MORB-eclogites or garnet pyroxenites (i.e. olivine-free, clinopyroxene-and garnet-bearing lithologies). Accounting for the variability in modal proportions of natural MORB-eclogites (75%Cpx + 25%Gt, Pertermann and garnet-bearing lithologies). MORB-eclogites have a bulk $D_{Zn/Fe}^{\text{MORB-eclogite}}$ of 0.73–0.76 and 0.49–0.63, respectively. Eclogites have a higher melt productivity and a lower solidus than dry peridotites (Kogiso, 2004; Leitch and Davies, 2001). Hence, if present in the source of OIB, they are expected to be about 60% molten for incipient melting (here F = 1%) of the surrounding peridotite mantle (Pertermann and Hirschmann, 2003). According to Eq. (2), melting of MORB-like eclogite (average Zn = 82 ppm and Zn/Fe = 9.4 × 104 for low-Gt MORB-eclogite, Inglis et al., 2017; average Zn = 198 ppm and Zn/Fe = 20.2 × 104 for high-Gt MORB-eclogite, John et al., 2010) will generate partial melts with 98-231 ppm of Zn and Zn/Fe of 13.4–31.6 × 104 after 60% melt extraction. Zinc concentrations and Zn/Fe ratios of modeled peridotite and MORB-eclogite derived melts (after 1 and 60% melting, respectively) thus encompass the entire range of OIB in good agreement with Le Roux et al. (2015). However, in a Zn vs Zn/Fe plot, the mixing curves between peridotite and low- or high-Gt MORB-eclogite melts are offset from the global trend of oceanic basalts (Fig. 4, yellow curves), predicting too high Zn/Fe ratios at a given Zn content. Zn/Fe positively correlates with Zn abundances of oceanic basalts ($R^2 = 0.87$, MORB and OIB) but not with their FeO$\text{Fe}$ content ($R^2 = 0.48$). Hence, the higher Zn/Fe observed in OIB compared to MORB is linked to Zn enrichment rather than Fe depletion. However, the lower bulk $D_{Zn/Fe}^{\text{source melt}}$ of MORB-eclogite relative to fertile peridotite (0.49–0.63 and 0.83–0.99, respectively) actually derives from distinct bulk Fe exchange coefficients ($D_{Zn/Fe}^{\text{MORB-eclogite}}$ = 1.32–1.55 and $D_{Zn/Fe}^{\text{peridotite}}$ = 0.79–0.90) rather than bulk Zn partitioning ($D_{Zn/Fe}^{\text{MORB-eclogite}}$ = 0.73–0.76 and $D_{Zn/Fe}^{\text{peridotite}}$ = 0.68–0.90, see Table 3). While the two independent observations that (1) Zn/Fe varies in oceanic basalts and (2) $D_{Zn/Fe}^{\text{source melt}}$ differs between peridotite and MORB-eclogite are perfectly accurate, they cannot be linked – a conclusion further supported by the global trend between Zn enrichment and radiogenic Sr-Nd isotope composition observed in oceanic basalts. We emphasize that all pyroxenites with composition spanning from peridotite to MORB-eclogite can also be ruled out as the source of Zn enrichment in OIB.

We also modeled the range of $\delta^{66}Zn$, $^{87/86}Sr$ and $^{143/144}Nd$ generated by melting-mixing of a fertile peridotite ($\delta^{66}Zn =$ +0.16 ± 0.06‰, $^{87/86}Sr =$ 0.72 ppm, $^{143/144}Nd =$ 5.13 ppm, Sossi et al., 2018; Palme and O’Neill, 2007; Salters and Stracke, 2004) and MORB-eclogite (average $\delta^{66}Zn =$ +0.27 ± 0.08‰, $^{87/86}Sr =$ 64-216 ppm, $^{143/144}Nd =$ 13-23 ppm, John et al., 2010; Inglis et al., 2013; Inglis et al., 2017; John et al., 2010) sources. Resulting mixing curves are systematically offset from the oceanic basalt array (Figs. 3a, b and 5, yellow curves). Neither peridotite melt ($\delta^{66}Zn =$ +0.23‰, $^{87/86}Sr =$ 0.70 ppm and $^{143/144}Nd =$ 5.13ppm, Salters and Stracke, 2004) nor MORB-eclogite melt ($\delta^{66}Zn =$ +0.26 ± 0.02‰, $^{87/86}Sr =$ 0.70 ppm and $^{143/144}Nd =$ 5.13ppm) can produce the heavy $\delta^{66}Zn$ and Sr-Nd isotope composition associated to the high Zn content of OIB (up to $\delta^{66}Zn =$ +0.49‰, $^{87/86}Sr =$ 0.70 ppm and $^{143/144}Nd =$ 5.12ppm).

### 3.4. Subducted sediment input

Oceanic basalts are usually classified according to their affinity to hypothetical mantle reservoirs, such as the depleted MORB-mantle (DMM), a high $^{238}U$/$^{204}Pb$ reservoir (HIMU) and distinct varieties of enriched mantle (EM I and II, Zindler and Hart, 1986; Willbold and Stracke, 2006; Stracke et al., 2005; Hofmann, 1997). It is also widely accepted that these mantle end-members reflect, in part, the involvement of recycled sediments in the source of OIB (Hofmann and White, 1982; Weaver, 1991). On a single trench basis, subducting sediments exhibit substantial geochemical variability. Using the Global Subducting Sediment (GLOSS) composition of Plank (2014) would not capture this heterogeneity in our mixing model. Instead, we take the most Zn-poor (Mariana trench: Zn = 64 ppm, Zn/Fe = 15.5 × 10$^4$, Sr = 161 ppm, Nd = 21.0 ppm, $^{87/86}Sr =$ 0.70617 and $^{143/144}Nd =$ 0.51252) and Zn-rich (Lesser Antilles trench: Zn = 124 pm, $^{87/86}Sr =$ 0.70260 and $^{143/144}Nd =$ 0.51307)
To our knowledge, the only Zn are ~90% molten at the locus of dry, fertile peridotite melting constraints from Spandler et al., 2010 indicate that anhydrous metapelites comparison in Appendix 4 but does not alter the following conclusions. Table 1 and Appendix 1, 2 for the whole dataset and references and Appendix 4 for modeling results. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Zn concentration (ppm) vs $\delta^{66}$Zn (‰) in oceanic basalts. Also shown are mixing curves between peridotite and sediments (brown curves and light brown field), MORB-eclogite (yellow curves and light yellow field) and C-bearing eclogite (black curve and blue dots overlay for the Monte Carlo simulation). See Table 3, Appendix 1, and Appendix 4 for modeling results. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Zn/Fe = 22.3 x 10$^4$, Sr = 110 ppm, Nd = 30.6 ppm, $^{87}/^{86}$Sr = 0.71585 and $^{143/144}$Nd = 0.51197) sediments from the compilation of Plank (2014) as possible end-members. Experimental constraints from Spandler et al., 2010 indicate that anhydrous metapelites are ~90% molten at the locus of dry, fertile peridotite melting (~1440 °C at 3GPa, Hirschmann, 2000). To our knowledge, the only Zn partitioning data available for metapelites are from Grassi et al. (2012) and 143/144Nd space (Fig. 4). Similarly, both continental margin sediments and 143/144 Nd spaces. Based on these results, we argue that C-bearing eclogites from Ravna et al. (2017) present the only available dataset of Zn concentration and Sr-Nd isotopic composition of C-bearing eclogites from ultrahigh-pressure metamorphic terranes (n = 4). These samples contain ≥5% of carbonates and have been interpreted to be fragments of a deeply subducted slab. Most importantly, they fulfill all the geochemical requirements discussed in Section 3.2: extremely high Zn concentration (111 ± 9 pm) and Zn/Fe ratio (10.1 ± 1.7 x 10$^4$), radiogenic Sr ($^{87}/^{86}$Sr = 0.70638 and Sr = 132 ± 34 ppm) and unradiogenic Nd ($^{143}/^{144}$Nd = 0.51249 and Nd = 7.4 ± 3.5 ppm, Ravna et al., 2017) isotope signatures compared to unaltered peridotites and MORB-eclogites. Unfortunately, no Zn isotope measurements have been reported for C-bearing eclogites yet. Considering the apparent lack of $^{66}$Zn fractionation during prograde metamorphism and dehydration of the subducted crust (see Section 3.1.3), the Zn isotope composition of deep-sea marine and high-pressure carbonates associated with the metamorphic crust is presumed to remain unchanged during subduction. To estimate the $^{66}$Zn composition of such lithology, we assume that the bulk C-bearing eclogite is a mixture of 90–95% MORB-eclogite (Zn = 91 ppm and $^{66}$Zn = +0.27 ± 0.08‰, Gale et al., 2013; Inglis et al., 2017) and 5–10% high-pressure carbonates (Zn = 130 ppm and $^{66}$Zn = +0.91 ± 0.24‰, Li et al., 2014; Pichat et al., 2003; modal proportions after Ravna et al., 2017). Hence, we find a bulk $^{66}$Zn of +0.30 to +0.35‰ for C-bearing eclogites. Considering a mineral assemblage of 60%Cpx + 35%Mgt + 5%Carb and the corresponding mineral-melt exchange coefficients (Table 3, Ravna et al., 2017; Le Roux et al., 2015; Sweeney et al., 1995) we find a bulk $^{66}$Zn of 0.73 and 0.50, respectively. The solidus and melt productivity of C-bearing eclogites is less constrained than that of typical MORB-eclogites (see Yaxley and Brey, 2004; Hammouda, 2003; Dasgupta et al., 2004; Kiseeva et al., 2012 for further discussion). Here, we assume that C-bearing eclogites are 60% molten for incipient melting (here F = 1%) of the surrounding peridotite mantle. Hence, we simply mix the peridotite-derived melt with the composition of sediments subducting at the Mariana and Lesser Antilles trenches in our model. An alternative model using bulk partitioning coefficients of anhydrous metapelites at 8GPa (Grassi et al., 2012, Table 3) but have been determined at much higher pressure (8-22GPa). In the absence of experimental constraints in the P-T range of interest, we assume that sediments are completely molten for incipient melting (here F = 1%) of the surrounding peridotite mantle. Hence, we simply mix the peridotite-derived melt with the composition of sediments subducting at the Mariana and Lesser Antilles trenches in our model. An alternative model using bulk partitioning coefficients of anhydrous metapelites at 8GPa (Grassi et al., 2012, Table 3) is provided for comparison in Appendix 4 but does not alter the following conclusions. Resulting mixing arrays are systematically offset from the global trend defined by oceanic basalts (Figs. 3a, b and 4, brown curves and light brown field) predicting too high Zn/Fe ratio and $^{87}/^{86}$Sr, and too low $^{143}/^{144}$Nd at a given Zn content. While the Zn and Sr-Nd isotope composition of at least some OIB could be readily explained by a three-component melting-mixing model of peridotite, MORB-eclogite and sediment sources, this scenario is clearly ruled out in a Zn vs Zn/Fe space (Fig. 4). Similarly, both continental margin sediments ($^{66}$Zn = +0.07 ± 0.11, Little et al., 2016) and subducted metasediments ($^{66}$Zn = +0.06 ± 0.19, Inglis et al., 2017) display significantly lighter signatures than unaltered peridotites ($^{66}$Zn = +0.18 ± 0.06‰) and oceanic basalts ($^{66}$Zn up to +0.40‰). Incorporation of subducted sediments in the mantle source of OIB cannot produce a heavy $^{66}$Zn signature (Fig. 5). The latter outcome further precludes any three-component mixing between sediments, peridotite and MORB-eclogite derived melts.

3.5. Carbon-bearing oceanic crust recycling

A growing number of studies advocates for the presence of C-bearing eclogites as possible source lithologies responsible for major elements enrichment in OIB (Jackson and Dasgupta, 2008; Dasgupta et al., 2010). Given the large offset of $^{66}$Zn between unmetasomatized peridotites ($^{66}$Zn = +0.18 ± 0.06‰) and more heterogeneous marine carbonates ($^{66}$Zn = +0.91 ± 0.24‰, Pichat et al., 2003; +1.07 ± 0.14‰, Little et al., 2016; up to +0.79 and +0.87 ± 0.14‰, Maréchal et al., 2000; Kunzmann et al., 2013), Zn isotopes are particularly well suited to track the carbon cycle at large scale (Liu et al., 2016; Liu and Li, 2019; Debret et al., 2018a). To our knowledge, Ravna et al. (2017) present the only available dataset of Zn concentration and Sr-Nd isotopic composition of C-bearing eclogites from ultrahigh-pressure metamorphic terranes (n = 4). These samples contain ≥5% of carbonates and have been interpreted to be fragments of a deeply subducted slab. Most importantly, they fulfill all the geochemical requirements discussed in Section 3.2: extremely high Zn concentration (111 ± 9 pm) and Zn/Fe ratio (10.1 ± 1.7 x 10$^4$), radiogenic Sr ($^{87}/^{86}$Sr = 0.70638 and Sr = 132 ± 34 ppm) and unradiogenic Nd ($^{143}/^{144}$Nd = 0.51249 and Nd = 7.4 ± 3.5 ppm, Ravna et al., 2017) isotope signatures compared to unaltered peridotites and MORB-eclogites. Unfortunately, no Zn isotope measurements have been reported for C-bearing eclogites yet. Considering the apparent lack of $^{66}$Zn fractionation during prograde metamorphism and dehydration of the subducted crust (see Section 3.1.3), the Zn isotope composition of deep-sea marine and high-pressure carbonates associated with the metamorphic crust is presumed to remain unchanged during subduction. To estimate the $^{66}$Zn composition of such lithology, we assume that the bulk C-bearing eclogite is a mixture of 90–95% MORB-eclogite (Zn = 91 ppm and $^{66}$Zn = +0.27 ± 0.08‰, Gale et al., 2013; Inglis et al., 2017) and 5–10% high-pressure carbonates (Zn = 130 ppm and $^{66}$Zn = +0.91 ± 0.24‰, Li et al., 2014; Pichat et al., 2003; modal proportions after Ravna et al., 2017). Hence, we find a bulk $^{66}$Zn of +0.30 to +0.35‰ for C-bearing eclogites. Considering a mineral assemblage of 60%Cpx + 35%Mgt + 5%Carb and the corresponding mineral-melt exchange coefficients (Table 3, Ravna et al., 2017; Le Roux et al., 2015; Sweeney et al., 1995) we find a bulk $^{66}$Zn of 0.73 and 0.50, respectively. The solidus and melt productivity of C-bearing eclogites is less constrained than that of typical MORB-eclogites (see Yaxley and Brey, 2004; Hammouda, 2003; Dasgupta et al., 2004; Kiseeva et al., 2012 for further discussion). Here, we assume that C-bearing eclogites are 60% molten for incipient melting (here F = 1%) of the surrounding peridotite mantle. Thus capable of generating high Zn concentrations (~125 ppm) asso...
curves allow us to estimate the fraction of peridotite and C-bearing eclogite melts required to generate the Zn enrichment of OIB. Most of their Zn composition can be explained with a 20:80 to 80:20 mix of melts from a peridotite and C-bearing eclogite source, respectively (e.g., Fig. 3a, b). C-bearing eclogites have higher melt productivity and a lower solubil than dry peridotites, contributing more to the final hybrid melt (Kogiso, 2004; Leitch and Davies, 2001). Hence, their true proportion in the source of OIB \((X_{\text{C-bearing eclogite}})\) can be inferred using the equation from Le Roux et al. (2011):

\[
X_A = \frac{(f_A \times 100) + f_B}{f_A + f_B}
\]

where \(f_A, f_B\) is function of the fraction of melt \((f_A, f_B)\) and degree of melting \((f_A, b)\) of the source components A and B \((f_A, b = f_A, b \text{ melt} / f_A, b)\) in the hybrid melt. The 20:80 and 80:20 mixes mentioned above correspond to 0.4–6% of C-bearing eclogite in the source of OIB. The density of eclogites varies with their carbon content, slightly decreasing from 3500 kg/m\(^3\) in typical MORB-eclogite to 3447.5 kg/m\(^3\) in MORB-eclogite containing 5 wt% CO\(_2\) (Pertermann and Hirschmann, 2003; Sanchez-Valle et al., 2011). In any case, eclogites are significantly denser than the surrounding peridotite mantle \((\rho_{\text{peridotite}} = 3300 \text{ kg/m}^3, \text{Pertermann and Hirschmann, 2003})\). The capacity of mantle plumes to carry C-bearing eclogites results from the competitive effect of their compositional (e.g., the proportion of dense material in the plume) and thermal (e.g., thermal anomalies compared to the surrounding mantle) buoyancies (Davies, 2011). Hence, the variable proportion of C-bearing eclogites required to explain the range of Zn enrichment in OIB could either reflect (1) the heterogeneous distribution of recycled material in the mantle, or (2) distinct plume thermal anomalies, or both. To assess the viability of the latter hypothesis, we estimated the average temperature of magma generation of MORB and OIB (1 bar liquidus temperature, Table 1) using the thermometer of Lee et al. (2009). While Zn partitioning varies little with changes in temperature (bulk \(D_{\text{Zn, low-}\text{peridotite} \rightarrow \text{melt}} = 0.88\) and \(D_{\text{Zn, high-}\text{peridotite} \rightarrow \text{melt}} = 0.82\), Le Roux et al., 2011) we find a striking positive correlation between the temperature of magma generation and their average Zn content (Fig. 6a, \(R^2 = 0.82\)) supporting a link between thermal anomalies and the proportion of C-bearing eclogite in the plume. This observation is tempered by the Hawaiian case which is by far the most buoyant hotspot (Steinberger, 2000; King and Adam, 2014). Temperatures are also given in terms of temperatures excess relative to the average temperature of \(-1400 \text{ °C}\) calculated for MORB \((\Delta T \text{ in °C, top axis})\). Also shown is the maximum proportion of C-bearing eclogite in the plume \((X_{\text{C-bearing eclogite}})\) at a given \(\Delta T\) to preserve a positive plume buoyancy using coefficients of thermal expansion of 2, 3, 4 and 5.10\(^{-5}\) °C\(^{-1}\) (blue curves, see text for details). In figure (b), MORB are represented as a neutral buoyancy \((i.e., 0 \text{ Mg/s}^2)\). See Table 1 for data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.7. Implications and perspectives for the Deep Carbon Cycle

Over the past few years, lot of attention has been given to the deep carbon cycle, arguing whether or not, long term carbon cycling is in equilibria between mantle carbon degassing, through partial melting and magmatic degassing processes, and deep recycling into the mantle by subduction (e.g., Kelemen and Manning, 2015 and references therein). These discrepancies emphasize the difficulty in determining the extent to which carbon (present in the form of inorganic and organic compounds) is mobilized in slab derived fluids during subduction, and whether some of this carbon may return to the deep mantle.

As demonstrated here and in previous studies (e.g., Eguchi et al., 2020), the composition of OIB involve melting of C-bearing recycled crustal components in the convecting mantle, and can place new constraints on the role of subduction on deep carbon recycling over geological times. Although C or CO\(_2\) data for oceanic basalts and especially OIB remain scarce, studies have shown that CO\(_2\)/Rb and CO\(_2\)/Ba ratios are constant in undegassed samples (Hauri et al., 2018; Cartigny et al., 2008; Shimizu et al., 2016). As such, Rb and/or Ba can be used as proxies for the primary CO\(_2\) content of oceanic basalts (Hauri et al.,
could be driven by modi
during subduction. In addition, these results point towards a deep recycling of carbon OIB. This clearly underlines a direct link between the amount of carbon respectively (Hauri et al., 2018). Depleted-MORB Mantle (DMM) estimates from (Fig. 7a, b). Zinc appears to be positively correlated to Rb (R² = 0.83) are expected to be driven by various inorganic (hydrated cation, hy-
amino acid) complexes (Fujii et al., 2011, 2014; Moynier et al., 2017).

The use of such systems in OIB have therefore the potential to reveal differentiation and degassing (e.g., Ca and Cu isotopes; Moynier et al., 2017; Breton, T., Nauret, F., Pichat, S., Moine, B., Moreira, M., Rose-Koga, E.F., Auclair, D., 2013. Geochemical heterogeneities within the Crozet hot-
ation during magmatic di

Changes in the long term carbon cycle through geological times could be driven by modification of the fraction of organic relative to inorganic carbon buried by subduction (e.g., Duncan and Dasgupta, 2017; Eguchi et al., 2020). Non-traditional stable isotope fractionations are expected to be driven by various inorganic (hydrated cation, hy-
droxide, chloride, sulfate, sulfide, phosphate) and organic (citrate, amino acid) complexes (Fujii et al., 2011, 2014; Moynier et al., 2017). The use of such systems in OIB have therefore the potential to reveal modifications on the nature of recycled carbon into the deep mantle throughout geological times. Given that both inorganic and organic carbon are expected to display isotopically light Zn signature (Fujii et al., 2014), the sole use of Zn isotopes cannot fully constrain the nature of this recycled carbon. Further investigations will required systematic data on OIB for both Zn and other stable isotopic tracers that are sen-
tive to carbon speciation and poorly a-
tected the

4. Conclusions

Zinc elemental and isotopic composition of oceanic basalts differs according to their tectonic settings, increasing from ridges to ocean islands. Unlike MORB, the high Zn and δ⁶⁸Zn recorded in OIB cannot be explained by partial melting of a fertile peridotite mantle source only. Importantly, global correlations between Zn content and Sr-Nd isotopes in oceanic basalts suggest that the Zn enrichment in OIB is inherited from a recycled component in their mantle source rather than melting processes.

We demonstrate that involvement of neither typical MORB-like oceanic crust nor subducted sediments can achieve the whole range of Zn composition in OIB. Instead, addition of 0.4–6% C-bearing oceanic crust to a fertile peridotite mantle fully resolves the Zn heterogeneity of OIB, both in terms of magnitude of Zn enrichment and global trends with Sr-Nd isotopes. Such scenario is corroborated by the elevated δ⁶⁸Zn of OIB relative to MORB and mantle peridotites, reflecting the contribution of isotopically heavy carbonates to the mantle source. Additionally, abundances of Zn and inferred primary CO₂ content of oceanic basalts are well-correlated which further supports the link between recycling of C-bearing subducted material and the amount of carbon in the source regions of OIB. Hence, Zn and δ⁶⁸Zn systematics may provide a valuable tool to fingerprint deep carbon cycling in the Earth’s mantle.

Finally, the positive correlation between Zn content and tempera-
ture of magma generation of oceanic basalts suggests that hotter mantle plumes are more likely to carry a higher proportion of dense C-bearing eclogite. Zn systematics therefore may provide evidence that the presence of heterogeneous domains in the source of OIB is linked to plume thermal buoyancy, bringing new insights into mantle dynamics.

Declaration of competing interest

None.

Acknowledgements

This research was supported by the F.N.R.S (Fond National de la Recherche Scientifique, Belgium) n 1141117F to HB. HB acknowledges his F.R.S.-F.N.R.S. research fellowship (Aspirant). The authors wish to thank J. De Jong (ULB) for technical support during MC-ICP-MS anal-
yses. We are grateful to the thorough and detailed reviews from Veronique Le Roux and Paolo Sossi and from the editor, Arturo Gomez-

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.epsl.2020.103174.

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