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Triple oxygen isotopic composition of the high-\(^{3}\text{He}/^{4}\text{He}\) mantle

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Abstract

Measurements of Xe isotope ratios in ocean island basalts (OIB) suggest that Earth’s mantle accreted heterogeneously, and that compositional remnants of accretion are sampled by modern, high-\(^{3}\text{He}/^{4}\text{He}\) OIB associated with the Icelandic and Samoan plumes. If so, the high-\(^{3}\text{He}/^{4}\text{He}\) source may also have a distinct oxygen isotopic composition from the rest of the mantle. Here, we test if the major elements of the high-\(^{3}\text{He}/^{4}\text{He}\) source preserve any evidence of heterogeneous accretion using measurements of three oxygen isotopes on olivine from a variety of high-\(^{3}\text{He}/^{4}\text{He}\) OIB locations. To high precision, the \(\Delta^{17}\text{O}\) value of high-\(^{3}\text{He}/^{4}\text{He}\) olivines from Hawaii, Pitcairn, Baffin Island and Samoa, are indistinguishable from bulk mantle olivine (\(\Delta^{17}\text{OBulk Mantle} - \Delta^{17}\text{OHigh 3He/4He olivine} = 0.002 \pm 0.004 (2\text{SEM})\‰\)). Thus, there is no resolvable oxygen isotope evidence for heterogeneous accretion in the high-\(^{3}\text{He}/^{4}\text{He}\) source. Modelling of mixing processes indicates that if an early-forming, oxygen-isotope distinct mantle did exist, either the anomaly was extremely small, or the anomaly was homogenised away by later mantle convection.

The \(\delta^{18}\text{O}\) values of olivine with the highest \(^{3}\text{He}/^{4}\text{He}\) ratios from a variety of OIB locations have a relatively uniform composition (\(~5\‰\)). This composition is intermediate to values associated with the depleted MORB mantle and the average mantle. Similarly, \(\delta^{18}\text{O}\) values of olivine from high-\(^{3}\text{He}/^{4}\text{He}\) OIB correlate with radiogenic isotope ratios of He, Sr, and Nd. Combined, this suggests that magmatic oxygen is sourced from the same mantle as other, more incompatible elements and that the intermediate \(\delta^{18}\text{O}\) value is a feature of the high-\(^{3}\text{He}/^{4}\text{He}\) mantle source. The processes responsible for the \(\delta^{18}\text{O}\) signature of high-\(^{3}\text{He}/^{4}\text{He}\) mantle are not certain, but \(\delta^{18}\text{O}/\delta^{87}\text{Sr}/\delta^{184}\text{Sr}\) correlations indicate that it may be connected to a predominance of a HIMU-like (high U/Pb) component or other moderate \(\delta^{18}\text{O}\) components recycled into the high-\(^{3}\text{He}/^{4}\text{He}\) source. Crown copyright © 2016 Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. INTRODUCTION

Noble gases provide evidence for the preservation of a reservoir in the Earth’s mantle that has been less melted and degassed than the rest of the mantle (as sampled by mid-ocean ridge basalts, (MORB)). Ocean island basalts from locations such as Iceland, Hawaii and Samoa provide

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evidence for a mantle component with a higher time-integrated $^{3}\text{He}/(U+\text{Th})$ ratio compared to the MORB mantle source (Kurz et al., 1982). This leads to the assumption that the inferred lower mantle source of high-$^{3}\text{He}/^{4}\text{He}$ OIB is less processed compared to the upper mantle, as typical mantle processing (i.e., melting, degassing, and recycling) acts to decrease $^{3}\text{He}/(U+\text{Th})$ (Kurz et al., 1982). This assumption is also supported by experimental work focused on understanding the behaviour of He compared to $U+\text{Th}$ during partial melting of the upper mantle (Jackson et al., 2013).

Isotopic systems with short-lived radioactive parent nuclides support the argument that the high-$^{3}\text{He}/^{4}\text{He}$ mantle source is in fact a compositional heterogeneity preserved from the Earth’s accretion. Specifically, a high-$^{3}\text{He}/^{4}\text{He}$ Icelandic basalt (DICE10; Mukhopadhyay, 2012) and a high-$^{3}\text{He}/^{4}\text{He}$ basalt from the Lau Basin (Peto et al., 2013) have lower, less radiogenic $^{129}\text{Xe}/^{130}\text{Xe}$ compared to the MORB mantle source, as previously discussed by Trieloff et al. (2000). The short half-life of $^{129}\text{I}$ ($^{129}\text{I}$ decays to $^{129}\text{Xe}$, $T_{1/2} = 15.7$ Ma) requires that the mantle sources of the DICE10 and Lau Basin samples were isolated from MORB mantle within 80 Ma of calcium–aluminium-rich inclusion (CAI) condensation. Apparently, this early-forming isotopic heterogeneity has not been completely homogenised, indicating relatively long timescales for complete mantle mixing (Mukhopadhyay, 2012; Peto et al., 2013).

Recent observations of $^{182}\text{W}/^{184}\text{W}$ heterogeneity associated with ancient plumes and other Archean rocks also support the possibility that the lower mantle contains reservoirs formed during Earth’s accretion (Touboul et al., 2012). Crucially, the $^{182}\text{W}/^{184}\text{W}$ heterogeneity observed for Earth is contrasted by $^{182}\text{W}/^{184}\text{W}$ homogeneity for the Moon (Touboul et al., 2007), suggesting that early-forming reservoirs were not homogenised during the giant impact phase of accretion. A late-forming Moon (formation after the extinction of $^{182}\text{Hf}$, >50 Ma after CAIs), and hence a late addition of cosmochemically distinct material to Earth, is supported by the age of the oldest lunar zircon (4.417 Ga; Nemchin et al., 2009), the oldest concordant age of lunar anorthosites (4.47 Ga; Nyquist et al., 2010), and the late model ages for the co-differentiation of major lunar geochemical reservoirs (low-Ti mare, high-Ti mare, KREEP, ~4.4 Ga after CAI; McLeod et al., 2014 and references within). We use the term “cosmochemically distinct” to refer to materials with distinct nebular feeding zones, which should result in correspondingly distinct $\Delta^{17}\text{O}$ values. Recent modelling efforts also suggest that giant impacts do not necessarily result in whole-mantle homogenisation (Nakajima and Stevenson, 2015).

If such an early-forming reservoir exists, it follows that this reservoir might also have a distinct O isotope composition compared to the rest of the mantle, given the timescales associated with Earth’s accretion, i.e., the Moon-forming impactor impacted Earth >50 Ma after CAI formation (Touboul et al., 2007). Oxygen possesses three stable isotopes: $^{16}\text{O}$, $^{17}\text{O}$ and $^{18}\text{O}$ and these were fractionated by a non-mass dependent process in the solar nebula, producing distinct reservoirs that do not fall along a mass fractionation line (Clayton, 1993; McKeegan et al., 2011).

Meteoritic materials generally display large non-mass dependent variations in O isotope compositions (quantified as variations in $\Delta^{17}\text{O}$), when compared to terrestrial samples (Clayton, 1993; Greenwood et al., 2005; Franchi, 2008). Even at a planetary scale, the distinct O isotopic composition of Martian rocks compared to terrestrial materials (Franchi, 2008) suggests that the inner solar system was not completely homogenised with respect to O isotopes. Given that terrestrial planets represent a stochastic mixture of nebular materials (Chambers, 2001; Kaib and Cowan, 2015), this also implies that material accreted to Earth and other terrestrial bodies, such as the Moon-forming impactor, had a range of O-isotope compositions, i.e., they were cosmochemically distinct. If the short-lived Xe isotopic compositions of high-$^{3}\text{He}/^{4}\text{He}$ OIB are evidence for an unmixed primordial heterogeneity, then it is likely that this heterogeneity also had a non-zero $\Delta^{17}\text{O}$ upon formation. That is, high-$^{3}\text{He}/^{4}\text{He}$ OIB should have O isotopes that fall off the TFL if subsequent interactions with the rest of the mantle were sufficiently small. Since oxygen is a major element, it mixes linearly between silicate reservoirs and has well constrained homogenisation tendencies compared to elements such as Xe or W, which are also potential tracers of materials isolated early in solar system history.

Previous studies of O isotope variation in high-$^{3}\text{He}/^{4}\text{He}$ material have focused almost entirely on measuring $\delta^{18}\text{O}$ and not $\delta^{17}\text{O}$, thus precluding the unambiguous identification of cosmochemical distinctions. A low-$\delta^{18}\text{O}$ component is commonly associated with plumes displaying high-$^{3}\text{He}/^{4}\text{He}$ signatures with the ultimate cause of low-$\delta^{18}\text{O}$ signatures having been variably attributed to source properties (Macpherson et al., 2000, 2005) or near-surface contamination (Wang and Eiler, 2008). If high-$^{3}\text{He}/^{4}\text{He}$ mantle has a $\delta^{18}\text{O}$ signature distinct from MORB mantle, this might indicate a fundamentally different history for these two reservoirs, potentially related to the distribution of materials recycled in to the mantle.

Here we test the hypothesis that high-$^{3}\text{He}/^{4}\text{He}$ mantle formed with a distinctive O isotopic signature and has not been completely homogenised since. Measurements of both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ have been made, allowing for the determination of $\Delta^{17}\text{O}$ in olivine from a variety of high-$^{3}\text{He}/^{4}\text{He}$ locations, including in samples from Bafﬁn Island and West Greenland (BI-WG) that exhibit the highest $^{3}\text{He}/^{4}\text{He}$ measured to date (Stuart et al., 2003; Starkey et al., 2009).

### 2. MATERIALS AND METHODS

#### 2.1. Samples

The olivine samples obtained for this study are from lava ﬂows from a range of locations including Bafﬁn Island and West Greenland (proto-Iceland plume), Hawaii, Samoa and Pitcairn. These locations were chosen because they are known for having lava ﬂows characterised by high $^{3}\text{He}/^{4}\text{He}$, and cover a wide range of locations across the
The BI-WG olivine samples are from picritic lava flows (except BI/CS/7, which is a dyke sample) that are thought to be stratigraphically equivalent, originating from the proto-Iceland plume that erupted 62–58 Ma. It has been shown previously that the Baffin Island dyke sample, BI/CS/7, has experienced a small amount of crustal contamination (Starkey et al., 2009) evidenced by its more enriched Sr and Nd isotopes compared to the rest of the sample suite. The Baffin Island (BI) samples, BI/CS/7 and BI/FPI/27, and West Greenland (WG) samples, 400485 and 400230, have not previously been measured for O isotopes but a large range of geochemical data for these samples is presented in Stuart et al. (2003), Starkey et al. (2009, 2012).

The Hawaiian olivines were extracted from samples HSDP2-SR0036-1.22, HSDP2-SR0741-7.90 and HSDP2-SR964-4.31 collected in the Hawaii Scientific Drilling Project. HSDP2-SR741-7.90 and HSDP2-SR964-4.30 have been measured for O isotopes by Wang et al. (2003), helium isotope data for all samples is presented in Kurz et al. (2004), and Sr and Nd isotope data in Bryce et al. (2005).

The Samoan olivines were extracted from samples OFU.04.03 (ankaramite dyke), OFU.04.14 (cumulate), OFU.04.15 (ankaramite) and OFU.04.17 (gabbro). These samples were collected from a range of locations in the OFu and Olosega islands, in the eastern province of the Samoan archipelago (Jackson et al., 2007). He, Sr, and Nd data for these samples are presented in Jackson et al. (2007). Sr isotopes and δ18O have previously been measured for OFU.04.17 by Workman et al. (2008).

The Pitcairn olivines were extracted from samples Pitcairn 8 and Pitcairn 16 collected from the Tedsite volcanic formation (Garapic et al., 2015). The helium isotope data for these samples is presented in Garapic et al. (2015).

The Icelandic olivines are from sample SK1 which is a Tertiary picrite from Selidarlu in NW Iceland. Olivines from this sample have a 3He/4He value of 37 Ra (Ellam and Stuart, 2004).

In the case of Hawaii, Samoa and Pitcairn, new aliquots of crystals from the same samples that had previously been measured for helium were analysed for their O isotope ratios whereas for BI-WG the same olivine samples that had been analysed by crushing for He were used for the O isotope analyses. The average 3He/4He values for the BI-WG samples in this study is 44 Ra, the average for Samoan samples is 26 Ra, for Hawaii it is 15 Ra and for Pitcairn it is 12 Ra (all data available in Table 1).

2.2. Oxygen isotope measurements

Oxygen isotope analyses were carried out at the Open University using an infrared laser-assisted fluorination system (Miller et al., 1999). Each replicate analysis was undertaken using approximately 2 mg of crushed olivine crystals that were hand-picked under a binocular microscope. Oxygen was released from the sample by heating in the presence of BrF₅. After fluorination, the released oxygen gas was purified by passing it through two cryogenic nitrogen traps and over a bed of heated KBr. Oxygen gas was analysed using a MAT 253 dual inlet mass spectrometer. Interference at m/z = 33 by the NF₅ fragment ion NF⁺ was monitored by performing scans for NF₂⁺ on all samples run in this study. In all cases NF₂⁺ was either negligible or absent. Recent levels of precision obtained on the Open University system, as demonstrated by 38 analyses of an internal obsidian standard were as follows: ±0.053‰ for δ17O; ±0.095‰ for δ18O; ±0.018‰ for Δ17O (2 SD), with full results available in supplementary information.

Oxygen isotopic analyses are reported in standard δ notation, where δ18O has been calculated as: $\delta^{18}O = \left(\frac{^{18}O/^{16}O_{sample}}{^{18}O/^{16}O_{ref}} - 1\right) \times 1000$ (‰) and similarly for δ17O using the $^{17}O/^{16}O$ ratio. Δ17O, which represents the deviation from the terrestrial fractionation line, has been calculated using a linearised format:

$$\Delta^{17}O = 1000 \ln(1 + \frac{^{17}O}{^{18}O}) - \lambda \times 1000 \ln(1 + \frac{^{18}O}{^{16}O})$$

where $\lambda = 0.5247$, which was determined using 47 terrestrial whole-rock and mineral separate samples (Miller et al., 1999). When calculating Δ17O values, Pack and Herwartz (2014) have advocated abandoning the use of slope values ($\lambda$) calibrated using natural silicate minerals and instead propose a significantly steeper slope of 0.5305, the theoretical maximum for equilibrium fractionation, with a y axis offset of 0. This approach is problematic in view of the fact that a wide range of studies demonstrate that the majority of natural silicates on Earth plot on slopes which vary between 0.5240 and 0.5250 (Miller et al., 2015). Here we retain the use of a $\lambda$ value of 0.5247 as this is based on well constrained analytical data (Miller et al., 1999; Miller, 2002). For the Δ17O comparisons reported here, the importance of choosing the proper $\lambda$ is minimised because we compare Δ17O values of samples with very similar δ18O values.

In this paper we are concerned with comparing the mean isotopic values, i.e., δ18O and Δ17O, of mantle reservoirs that may have potentially remained isolated from each other since Earth accretion. In order to indicate the level of uncertainty of these mean values, the errors quoted throughout this paper, unless otherwise indicated, are two times the standard error of the mean (2 × SEM), where standard error of the mean (SEM) = standard deviation (SD)/$\sqrt{n}$ (where $n$ = number of measurements). Values for both the SD and SEM for all samples analysed in this study are given in Table 1.

During the course of this study both internal (obsidian) and international standards (UWG-2 garnet, NBS-28, San Carlos olivine) were run alongside the olivine samples. For reference, the full dataset obtained for UWG-2 garnet, NBS-28 and the internal obsidian standards, run over the course of this study, are included as a table in supplementary information. The average values we obtained for UWG-2 garnet and NBS-28 were δ18O = 5.78‰ and 9.59‰, which are extremely close to the recommended values (also available in table in supplementary information). In theory, San Carlos olivine would be the most appropriate standard for this study, being closest in mineralogical composition to the high 2He/4He olivine samples. Literature δ18O values for San Carlos range from 4.70‰ to 5.28‰, which is not a particularly wide variation when
Table 1
Triple oxygen isotope compositions as measured by laser fluorination for a range of samples from Iceland, Baffin Island, West Greenland, Hawaii and Samoa plus average values for these and for the standards San Carlos olivine and PSRI Obsidian. $^{3}He/^{4}He$ values measured in previous studies are provided as reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>n</th>
<th>$^{3}He/^{4}He$</th>
<th>$\delta^{18}O$‰</th>
<th>SD</th>
<th>SEM</th>
<th>$\delta^{16}O$‰</th>
<th>SD</th>
<th>SEM</th>
<th>$\Delta^{15}O$‰</th>
<th>SD</th>
<th>SEM</th>
<th>$\Delta^{13}O$‰</th>
<th>SD</th>
<th>SEM</th>
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<td>0.019</td>
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<td>-0.012</td>
<td>0.008</td>
<td>0.002</td>
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<td>0.011</td>
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<td>0.011</td>
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<td>0.103</td>
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<tr>
<td>San Carlos Olivine I ($\delta^{18}O = 4.88‰$)</td>
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<td>0.002</td>
<td>-0.012</td>
<td>0.010</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>San Carlos Olivine II ($\delta^{18}O = 5.23‰$)</td>
<td></td>
<td>9</td>
<td>2.674</td>
<td>0.054</td>
<td>0.018</td>
<td>5.130</td>
<td>0.096</td>
<td>0.032</td>
<td>0.007</td>
<td>0.010</td>
<td>0.003</td>
<td>-0.014</td>
<td>0.010</td>
<td>0.003</td>
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<td>PSRI Obsidian</td>
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<td>39</td>
<td>3.808</td>
<td>0.026</td>
<td>0.004</td>
<td>7.267</td>
<td>0.047</td>
<td>0.007</td>
<td>0.029</td>
<td>0.009</td>
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<td>Average values</td>
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<td>2.619</td>
<td>0.037</td>
<td>0.004</td>
<td>5.017</td>
<td>0.071</td>
<td>0.008</td>
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<td>0.002</td>
<td>0.000</td>
<td>-0.011</td>
<td>0.002</td>
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<tr>
<td>&quot;Bulk Mantle&quot; $\delta^{18}O$‰ (Mattey et al., 1994)</td>
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<td>5.18</td>
<td>0.14</td>
<td>0.02</td>
<td>0.012</td>
<td>0.01</td>
<td>0.002</td>
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<tr>
<td>&quot;Bulk Mantle&quot; $\Delta^{15}O$‰ (Average San Carlos I and II)</td>
<td></td>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

Notes:
SD = sample standard deviation.
SEM = standard error of the mean.
SEM was calculated as: SEM = SD/$\sqrt{n}$.
n = number of measurements.
$\Delta^{15}O$ = $\delta^{15}O - 0.52 \delta^{18}O$.
Linearized value: see text for details.
compared to other standards (UWG-2 garnet, NBS-28 quartz, NBS-30 biotite) (Kusakabe and Matsuhisa, 2008). Such variation would normally be ascribed to inter-laboratory analytical differences. However, San Carlos olivine is not a homogenous standard and distinct isotopic varieties exist (Thirlwall et al., 2006), which may be related to the mineralogy or metasomatic history of the particular nodule sampled from the San Carlos locality. For this study we obtained two samples of San Carlos olivine, a low δ18O variety, referred to as San Carlos I by Thirlwall et al. (2006), with a δ18O value of 4.88‰ (Mattey and Macpherson, 1993) and a high δ18O variety, San Carlos II, assigned a value of δ18O = 5.22‰ by Thirlwall et al. (2006). The results of our analysis of San Carlos I and II are given in Table 1. Nineteen analyses of San Carlos I gave a δ18O value of 4.768 (±0.060)‰, which is just over 0.1‰ lower than the value of δ18O = 4.88‰ obtained by Mattey and Macpherson (1993). Nine replicate analyses of San Carlos II gave a δ18O value of 5.130 (±0.064)‰, which is just under 0.1‰ lower than the assigned value quoted by Thirlwall et al. (2006). However, the five analyses of San Carlos II given in Table 3 of Thirlwall et al. (2006) have a mean value of 5.19 (±0.06)‰, which indicates that the apparent offset between our analysis of San Carlos II and that of Thirlwall et al. (2006) is probably not statistically significant. It would appear that further work is required to adequately assess the use of San Carlos as a reliable interlaboratory isotopic standard. However, despite San Carlos olivine not being a well-characterised international standard, the close compositional match between it and the olivines analysed in this study make it a useful standard with respect to Δ17O.

3. RESULTS

3.1. O isotopes in high-3He/4He samples

Despite their differing δ18O values, the two fractions of San Carlos olivine measured in this study (San Carlos I and II) both have identical Δ17O values within error (Table 1). Furthermore, the recent study of Pack and Herwartz (2014) indicates that San Carlos olivine lies along a common mass fractionation line with the other minerals within San Carlos xenoliths and MORB glass (Pack and Herwartz, 2014). This suggests that San Carlos olivine can be used as a proxy for the Δ17O of the bulk mantle. We use the term “bulk mantle” to denote the mantle other than high-3He/4He mantle. For the δ18O measurements we also plot the average mantle value reported by Mattey et al. (1994) of 5.18 ± 0.28‰ (n = 76, 2 S.D.) (Table 1) to provide a frame of reference.

Fig. 1 displays the new Δ17O and δ18O measurements for olivines from a range of locations with variable 3He/4He ratios up to 47.6 Ra. High-3He/4He olivines show no deviation from the bulk mantle mean Δ17O value (within 2σ SEM), as defined by replicate analyses of San Carlos olivine. To high precision, there is no resolvable difference between the Δ17O average of San Carlos olivine and the Δ17O average of high 3He/4He olivine (Fig. 1, Δ17O San Carlos olivine – Δ17O high 3He/4He olivine = –0.002 ± 0.004‰). A Baffin Island sample (BI/CS/7) is the only one to fall off the main trend, to a positive value of Δ17O and this measurement also has a larger error than the other samples.

High-3He/4He olivines are defined here as samples with >20 Ra, >4.75 δ18O, and show no indications of crustal contamination (Table 1) and display a narrow range of δ18O values (Fig. 1b). If olivines with an Ra value of <20, δ18O < 4.75‰ (SK1), and indications of crustal contamination (BI/CS/7) are excluded, our remaining 74 analyses of high-3He/4He olivines have a mean δ18O value of 5.017 (±0.016)‰ (Table 1). The average δ18O value of the average mantle and high-3He/4He olivines are significantly different (2-sample T-test p value = 0.002). The samples in the high-3He/4He group cover nearly the entire range of
locations in this study, including Iceland, BI-WG, Samoa and Hawaii. The Icelandic sample (SK1) is noted to display particularly low $\delta^{18}O$, a feature which has previously been discussed by Macpherson et al. (2005) and is explained by interaction of the Icelandic melts with high-latitude, low $\delta^{18}O$ meteoric water. Sample BI/CS/7 is also suggested to be affected by crustal contamination (Starkey et al., 2009). As such, these samples do not likely represent a primary melt of their mantle source and are excluded from calculations related to the composition of the high-3He/4He reservoir (Table 1).

Coupled $^3$He/$^4$He–$\delta^{18}O$ measurements on olivine (this study and published data, see Supplementary information for references) from a range of geographic/geochemical affinities (Iceland, Hawaii, Pitcairn, Samoa, HIMU-affinity, and “other”) are presented in Fig. 2 to further explore the He–O isotope systematics. We use the term HIMU-affinity because many of the locations with coupled He–O–Pb isotopic measurements have elevated $^{206}$Pb/$^{204}$Pb values but do not approach the global endmember. The highest $^3$He/$^4$He olivines from a variety of geographic/geochemical affinities have a narrow range of $\delta^{18}O$ values, despite a wide range of $\delta^{18}O$ values observed for lower $^3$He/$^4$He olivines. This convergence of $\delta^{18}O$ values at high $^3$He/$^4$He is observed both within individual geographic/geochemical affinities (Iceland and Hawaii, Fig. 2a and b) and in the global compilation (Fig. 2g). There is evidence for a small $\delta^{18}O$ displacement of high-$^3$He/$^4$He olivines to values lower than mean mantle olivine (solid vertical lines, Fig. 2, Mattey et al., 1994). The distinction between high-$^3$He/$^4$He materials (olivines and olivine equivalent glasses, >20 Ra and >4.75 $\delta^{18}O$, this study and published data) and mean mantle olivine is also statistically significant (2-sample $T$-test $p$ value = 0.00003). However, this result should be treated with some caution because of potential interlaboratory issues and the variability of San Carlos olivine as a reference material.

4. DISCUSSION

4.1. Transfer of oxygen from high-$^3$He/$^4$He mantle source to high-$^3$He/$^4$He magmatic olivine

Magmatic $^3$He/$^4$He signatures are commonly quantified by measuring the composition of He released from olivine-hosted inclusions during crushing, while corresponding O isotopic compositions of olivines are measured on the bulk grain. Because the He and O measurements are not from the exact same material (inclusions vs. bulk olivine), and because He and O have variable sensitivity to crustal contamination and mixing, it is not required that high-$^3$He/$^4$He olivines contain significant quantities of O derived from the high-$^3$He/$^4$He mantle source. If true, O isotopic values would be essentially decoupled from $^3$He/$^4$He values and provide little information regarding the nature of the high $^3$He/$^4$He source.

Several lines of evidence argue that O and He remain coupled through magma genesis and melt migration processes. Despite the tendency for olivine to trap magmatic He and O relatively early in the crystallisation process, it is possible that He and O in a primary melt are principally derived from two unrelated mantle sources. Helium is highly incompatible in upper mantle solids (Heber et al., 2007; Jackson et al., 2013) and is correspondingly concentrated in small degree mantle melts. These small degree melts can migrate from their source and hyperbolically mix with other mantle materials. In this mixing scenario, the He isotopic composition of the resulting material will be dominated by the incompatible element-enriched, low degree melt, while the major element composition of the material will be dominated by the volumetrically major mixing component. If He is decoupled from less incompatible elements through low degree melts or other hyperbolic mixing processes, it is expected that high-$^3$He/$^4$He materials will have highly variable Sr, Nd, Pb, and O isotopic compositions. Whereas, if He remains coupled to less incompatible elements through melt production and migration processes, it is expected that high-$^3$He/$^4$He materials from a given location will cluster in a restricted range of Sr, Nd, Pb, and O isotopic space. Broad correlations between $^3$He/$^4$He and radiogenic isotope values ($^{87}$Sr/$^{86}$Sr, $^{143}$Nd, $^{206}$Pb/$^{204}$Pb) have previously been identified (Hart et al., 1992, Supplementary information), although this relationship does not always hold within specific regional groups (e.g., BI-WG, Starkey et al., 2009, 2012). However, the fact that high-$^3$He/$^4$He olivine from a wide variety of geographic/geochemical affinities share similar isotopic compositions for Sr, Nd, Pb, and O isotopic space (Hart et al., 1992, Supplementary information), although this relationship does not always hold within specific regional groups (e.g., BI-WG, Starkey et al., 2009, 2012). This result is consistent with previous attempts to detect $\Delta^{17}O$ anomalies in Precambrian rocks relative to modern rocks (Robert et al., 1992; Rumble et al., 2013).

There are a number of scenarios that could account for homogenous $\Delta^{17}O$ values throughout the solid Earth. Scenario 1 is that the Earth underwent homogenous O isotope accretion, resulting in no difference between the $\Delta^{17}O$ composition for early-formed mantle reservoirs and bulk mantle. Although our results are consistent with such a model, this model is not supported by the range of O isotope compositions measured in the inner solar system.

4.2. $\Delta^{17}O$ composition of high-$^3$He/$^4$He olivine

The main observation of this study is that the $\Delta^{17}O$ composition of high-$^3$He/$^4$He olivines is indistinguishable from the $\Delta^{17}O$ composition of the bulk mantle to high precision, where the bulk mantle $\Delta^{17}O$ value is defined by San Carlos olivine (Table 1). This suggests that post-accretion processes have effectively homogenised primordial major element heterogeneities, or that such heterogeneities were small or non-existent to begin with (e.g., Dauphas et al., 2014; Mastrobuono-Battisti et al., 2015). This result is consistent with previous attempts to detect $\Delta^{17}O$ anomalies in Precambrian rocks relative to modern rocks (Robert et al., 1992; Rumble et al., 2013).
and our current dynamical understanding of accretion (Kaib and Cowan, 2015). Thus, it seems unlikely that the Earth would have accreted homogenously in terms of O isotopes, a concept which is supported by Herwartz et al. (2014).

On the other hand, the data obtained in this study can be used to test a number of heterogeneous O isotope accretion possibilities. Scenario 2 involves isolation of the high-He/4He source prior to the cessation of accretion (i.e., prior to the Moon-forming impact) followed by later extensive homogenisation between it and the bulk mantle. Scenario 3 involves isolation of the high-He/4He source following the end of accretion and homogenisation of Earth (after the last significant shift of bulk mantle δ18O – i.e., after the Moon-forming impact, or potentially the late veneer). As it is not clear exactly what process formed the high-He/4He reservoir, in these models we use ‘isolation’ in general terms to describe the early chemical isolation of high-He/4He mantle, as required by short-lived Xe isotopic measurements (Mukhopadhyay, 2012; Peto et al., 2013) and suggested by short-lived W isotopic measurements (Touboul et al., 2012).

Here we introduce a two-stage mixing model in support of Scenario 2. The standard model for the formation of the

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**Fig. 2.** 3He/4He-δ18O measurements plotted by (a–f) geographic/geochemical affinities and (g) as a global compilation. The highest 3He/4He olivines with a variety of geographic/geochemical affinities have a narrow range of δ18O values, despite a wide range of δ18O values observed for lower 3He/4He olivine. This suggests He and O remain coupled during melt production and migration processes (see Section 4.1). Data points with surrounding circles have been converted to δ18O-olivine equivalent values using the mineral–mineral fractionations from Mattey et al. (1994) for clinopyroxene and Eiler et al. (2000a) for glass and plagioclase. All conversions are from glass to olivine except from the Gorgona and Galapagos data.
Moon has a Mars-sized impactor (10% of Earth’s current mass) colliding with the Earth (Canup, 2004). Mixing of a Moon-forming impactor with the bulk mantle would result in an intermediate $\Delta^{17}O$ composition that is determined by the relative masses and initial $\Delta^{17}O$ values of these two end-members. For example, if the bulk mantle was 85% of the present silicate Earth and equilibrated with a Mars-sized impactor (10% of present Earth mass) with Mars-like $\Delta^{17}O (\Delta^{17}O_{\text{Mars}} = 0.301‰, \text{Franchi et al., 1999})$, the resultant mixture would have a $\Delta^{17}O$ composition that is increased by 0.032‰. In this calculation, high-$^{3}\text{He}/^{4}\text{He}$ mantle occupies the remaining 5% of silicate Earth, and if not involved in the homogenisation with the impactor, would still have a $\Delta^{17}O$ value that is 0.032‰ lower than the bulk mantle. This difference in $\Delta^{17}O$ between the bulk mantle and the high-$^{3}\text{He}/^{4}\text{He}$ mantle is large and not observed given the present data, allowing this mixing scenario to be rejected.

An initially different $\Delta^{17}O$ composition for high-$^{3}\text{He}/^{4}\text{He}$ mantle, however, could be obscured if there was later exchange of materials between bulk mantle and high-$^{3}\text{He}/^{4}\text{He}$ mantle (i.e., a two-stage mixing model, Fig. 3). Modelling the exchange as an equal-mass process (no change in mass for either reservoir), homogenisation of the high-$^{3}\text{He}/^{4}\text{He}$ reservoir and bulk mantle must progress to at least 90%, given a limit of $+0.002/-0.004$‰ (2 SEM) for the difference in $\Delta^{17}O$ between the bulk mantle and high-$^{3}\text{He}/^{4}\text{He}$ mantle (Fig. 3). This same exchange results in a 0.001‰ decrease of $\Delta^{17}O$ for the bulk mantle. A change of 0.003‰ is the maximum allowable $\Delta^{17}O$ shift for bulk Earth, taking the Moon as a proxy for the initial O isotope composition of bulk Earth and the $\Delta^{17}O$ measurement of the Earth–Moon difference as calculated by Wiechert et al. (2001) (2 SEM), a difference which is in agreement with Hallis et al. (2010). Thus, this scenario can satisfy the available $\Delta^{17}O$ constraints for the Earth–Moon-high-$^{3}\text{He}/^{4}\text{He}$ mantle system and cannot be rejected.

However, it should be noted that there is some disagreement in the recent literature over the Earth–Moon difference, with one study (Herwartz et al., 2014) detecting a larger difference than that used in this modelling. This possibility is discussed below. By taking the Moon as a proxy for the initial O isotope composition of bulk Earth, we make the implicit assumption that oxygen was highly homogenised between these two bodies in the aftermath of the impact event.

Using the constraints provided by the similarity of $\Delta^{17}O$ in the Earth–Moon-high-$^{3}\text{He}/^{4}\text{He}$ reservoir system, we can determine permissible parameters for the mass of the high-$^{3}\text{He}/^{4}\text{He}$ reservoir, mass of the Moon-forming impactor, and the $\Delta^{17}O$ difference between the impactor and Earth (Fig. 3). These scenarios follow the same form as outlined in the example provided above.

For all these models, some degree of homogenisation of the high-$^{3}\text{He}/^{4}\text{He}$ reservoir and bulk mantle is needed to account for the similarity of their $\Delta^{17}O$ compositions, i.e., high-$^{3}\text{He}/^{4}\text{He}$ is not a closed system and cannot be regarded as strictly primordial at the major element level. For mixing calculations focused on exploring the effect of impactor $\Delta^{17}O$ composition (Fig. 3a) we adopt the more canonical approach of assuming a Mars-sized impactor (10% of present Earth, with a mantle/core mass ratio equal to present-day Earth) and assume the size of the high-$^{3}\text{He}/^{4}\text{He}$ reservoir to be 5% of the present-day mantle. If we take the $\Delta^{17}O$ composition of the impactor to be ±0.15‰ (i.e., the “mean $\Delta^{17}O$” difference between bulk mantle and giant impactors, as calculated by Pahelevan and Stevenson (2007)) then this scenario requires >60% homogenisation of the high-$^{3}\text{He}/^{4}\text{He}$ reservoir and bulk mantle to mute the difference in $\Delta^{17}O$ imparted between these reservoirs following the Moon-forming impact (Fig. 3a). In the case of extremely similar, or extremely different, $\Delta^{17}O$ values for bulk mantle, and the impactor, (i.e., an angrite-like or Mars-like impactor), >20% and >90%...
homogenisation, respectively, are required for the scenario parameters. The angrite-like and Mars-like impactor compositions are taken from Greenwood et al. (2005) and Franchi et al. (1999), respectively. Changing the mass of the high-3He/4He reservoir does not substantially affect the percentage of homogenisation required, holding other variables constant (Fig. 3b). For an impactor with a “mean Δ17O” composition, increasing the volume of the high-3He/4He reservoir from 1% to 40% of the mantle results in the homogenisation requirement changing from >60% to >75%.

Scenarios with impactors smaller than the canonical size require less homogenisation. Reducing the impactor mass from 10% to 5% of present Earth mass effectively halves the required amount of homogenisation (Fig. 3c). Larger impactors require increasing amounts of homogenisation for a given O isotope composition. If an impactor with “mean Δ17O” exceeds 40% of the present Earth mass, homogenisation of the high-3He/4He reservoir (5% of present-day mantle mass) and bulk mantle generates a corresponding Δ17O shift in the bulk mantle that is larger than the difference between the Earth and Moon as calculated by Wiechert et al. (2001) and Hallis et al. (2010), but smaller than the difference as calculated by Herwartz et al. (2014) (solid vertical lines, Wiechert et al., 2001, Fig. 3). Similarly, if the high-3He/4He reservoir exceeds (or previously exceeded) 20% of the present-day mantle mass, homogenisation of the high-3He/4He reservoir and the bulk mantle generates corresponding Δ17O shifts in the bulk mantle that are larger than the current difference between the Earth and Moon (vertical solid lines, Fig. 3b). Taking this scenario, homogenisation during the giant impact phase of Earth’s accretion appears to involve a large majority of the mantle, including both the upper mantle and majority of the lower mantle. This conclusion is dependent on the assumed Δ17O composition and size of the impactor. Smaller impactors, and with less distinct Δ17O compositions, allow for more of the mantle to have remained isolated.

It is worth noting that recent measurements of Δ17O for Moon and Earth materials yield a difference of +0.012 ± 0.006‰ (Herwartz et al., 2014), in disagreement with previous determinations (Wiechert et al., 2001; Hallis et al., 2010). If these newer measurements are robust, the lunar Δ17O composition no longer constrains the Δ17O composition of bulk mantle, to a specific value. Rather, a high lunar Δ17O value would suggest the impactor also had a relatively high Δ17O value. Following this, the terrestrial bulk mantle would have a relatively high Δ17O value compared to any early isolated reservoir. This potential scenario allows us to only consider the upper bound of the high-3He/4He reservoir Δ17O constraint (upper edge of grey boxes, Fig. 4), which is tighter than the lower bound. Only considering this upper bound, an impact scenario with an enstatite chondrite-like impactor (composition from Herwartz et al., 2014), which represents an impactor with an extremely similar Δ17O value to bulk mantle, still requires >40% homogenisation (Fig. 3b). A small, positive Δ17O difference between the Moon and Earth also requires that the formation of the Moon acted to shift Δ17O of the bulk mantle and that any early isolated reservoir, i.e., the high-3He/4He mantle, should have a relatively low Δ17O value, supporting the mixture modelling presented above.

In Scenario 3 we look at the possibility that the homogeneity of Δ17O in the solid Earth can be explained by isolation of the high-3He/4He mantle following the last addition of cosmochemically distinctive oxygen to Earth (i.e., after the Moon-forming impact). The time-window for this possibility is narrow, i.e., >50 Ma after, but <80 Ma after CAIs. This window is based on the likelihood that (1) the Moon-forming impact was associated with the delivery of anomalous O (as indicated by Herwartz et al. (2014) and analyses of other inner solar system materials) and occurred after the lifetime of 182Hf (i.e., >50 Ma after CAI; Touboul et al., 2007), and (2) the high-3He/4He reservoir was isolated within the lifetime of 129I (i.e., <80 Ma after CAI; Mukhopadhyay, 2012; Peto et al., 2013). In light of the evidence for Moon formation >100 Ma after CAI condensation (Nemchin et al., 2009; Nyquist et al., 2010; McLeod et al., 2014 and references within), and for the association of plumes with high 3He/4He and anomalous 182W/184W ratios (Touboul et al., 2012), we consider it more likely that high-3He/4He mantle was isolated prior to the end of Earth’s accretion (taken here to mean the giant Moon-forming impact) and that subsequent interactions with the bulk mantle have effectively obscured any distinctions in Δ17O (Scenario 2). It is also possible that the late veneer shifted the bulk mantle Δ17O composition as much as 0.02‰ (Herwartz et al., 2014). This exceeds the precision of the current study, also supporting Scenario 2.
A principal contention of Scenario 2 is that high-$^3$He/$^4$He mantle is not a pristine primordial reservoir. Rather, it is an early-forming reservoir that has experienced subsequent homogenisation with bulk mantle materials and that the degree of this homogenisation can be constrained using mixing models (Fig. 3). The possibility that high-$^3$He/$^4$He mantle is not a pristine primordial reservoir is supported by recent arguments for extensive amounts of recycling of modern atmospheric Xe into the high-$^3$He/$^4$He reservoir (~85% of total Xe in mantle source; Mukhopadhyay, 2012; Peto et al., 2013) and the differences in radiogenic isotopic composition observed between high-$^3$He/$^4$He locations globally (Jackson et al., 2007; Supplementary information). Thus, our findings add to the evidence for an open-system, high-$^3$He/$^4$He mantle source that is also robust to complete mixing over nearly the entirety of Earth's history. If the high-$^3$He/$^4$He mantle source is related to lower mantle structure (e.g., large low shear velocity provinces or ultra-low velocity zones), our findings also imply that these structures are not strictly primordial, rather they represent a combination of both early-forming materials and materials sourced from the Earth’s lithosphere. This possibility gains support from recent dynamical modelling efforts focused on understanding the interactions between large low shear velocity provinces and recycled materials (Li et al., 2014).

4.3. Implications for the $\delta^{18}$O values of high-$^3$He/$^4$He olivines

High-$^3$He/$^4$He olivines from a wide variety of locations appear to have a common $\delta^{18}$O composition near 5‰ (Fig. 2). Mass dependent O isotope variability can result from melting-crystallisation processes, source variations, and near-surface contamination. Samoa and Hawaii are located on top of thick lithosphere, which acts to truncate their melting column, concentrating lower degree melts from higher pressure and temperature regimes. The modern Iceland plume is associated with a rifting environment which promotes higher degree melts from lower pressure and temperature regimes. BI-WG are also associated with a rifting environment but here the proto-Iceland plume and temperature regimes. BI-WG are also associated with materials sourced from the Earth's lithosphere (Fig. 2). This observation, thus, points to a large role for HIMU-affinity materials or another recycled component with a $\delta^{18}$O similar to DMM, in explaining the open-system behaviour of high-$^3$He/$^4$He mantle (Albarede, 1998; Class and Goldstein, 2005; Garapic et al., 2015).

Global endmember HIMU materials do not have radiogenic $^{87}$Sr/$^{86}$Sr values and cannot explain the $^{87}$Sr/$^{86}$Sr variation observed between the high-$^3$He/$^4$He components expressed at different plume locations (Fig. 4). HIMU-like signatures are commonly observed within both MORB and OIB that have relatively radiogenic $^{87}$Sr/$^{86}$Sr values but more moderate $^{206}$Pb/$^{204}$Pb values (Stracke et al., 2005). Given the ubiquity of this material throughout the mantle, it has been suggested that it represents a component that is internal to the mantle tetrahedron, i.e., a HIMU-affinity FOZO, possibility related to recycled oceanic crust that is less modified by subduction compared to global endmember HIMU. This HIMU-affinity component is able to explain the $\delta^{18}$O, $^{87}$Sr/$^{86}$Sr variations between high-$^3$He/$^4$He components.

5. CONCLUSIONS

The mean $\Delta^{17}$O composition of olivines from non-crustally contaminated, high-$^3$He/$^4$He (>20 Ra, $\delta^{18}$O > 4.75‰) OIB is indistinguishable from mean mantle olivine to high precision, despite evidence for the early isolation of high-$^3$He/$^4$He mantle. We introduce 3 scenarios that can account for the similarity in $\Delta^{17}$O of the solid Earth: (1) homogenous O isotope accretion, (2) isolation
of the high-$^3$He/$^4$He source prior to the cessation of accretion and later extensive homogenisation between it and the bulk mantle or (3) isolation of the high-$^3$He/$^4$He source after the last significant shift of $\Delta^{17}$O in the bulk mantle. Scenario (2) is favoured, but regardless of which possibility correctly explains the homogeneity of $\Delta^{17}$O throughout the solid Earth, the results indicate that, to high precision, there is no evidence that the Earth contains cosmochemically distinct reservoirs for major elements.

Olivines with high-$^3$He/$^4$He values extracted from plume lavas have mean $\delta^{18}$O of $\sim$5‰. The fact that there is a narrow range of $\delta^{18}$O values associated with high-$^3$He/$^4$He olivines, and that, globally, there are correlations between $\delta^{18}$O and radiogenic isotopes (He, Nd, Sr, and Nd; see Fig. 2 and Supplementary information) implies that O remains coupled to the more incompatible elements during melt production and migration processes. The $\delta^{18}$O value for high-$^3$He/$^4$He materials may suggest that moderate $\delta^{18}$O materials (e.g., HIMU-affinity materials) are the dominant recycling components for high-$^3$He/$^4$He mantle.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.12.027.

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