



Triple oxygen isotope constraints on the origin of ocean island basalts

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Abstract Understanding the origin of ocean island basalts (OIB) has important bearings on Earth's deep mantle. Although it is widely accepted that subducted oceanic crust, as a consequence of plate tectonics, contributes material to OIB's formation, its exact fraction in OIB's mantle source remains ambiguous largely due to uncertainties associated with existing geochemical proxies. Here we show, through theoretical calculation, that unlike many known proxies, triple oxygen isotope compositions (i.e. $\Delta^{17}O$) in olivine samples are not affected by crystallization and partial melting. This unique feature, therefore, allows olivine $\Delta^{17}O$ values to identify subducted oceanic crusts in OIB's mantle source. Furthermore, the fractions of subducted ocean sediments and hydrothermally altered oceanic crust in OIB's mantle source can be quantified using their characteristic $\Delta^{17}O$ values. Based on published $\Delta^{17}O$ data, we estimated the fraction of subducted oceanic crust to be as high as 22.3% in certain OIB, but the affected region in the respective mantle plume is likely to be limited.

Keywords Triple oxygen isotope · Helium isotope · Ocean island basalts · Mantle plume · Mantle heterogeneity · Crustal recycling

1 Introduction

Earth is highly evolved and differentiated into different layers (Hofmann 1988). The surface layers of the Earth prevent us from directly observing its deep mantle. Ocean island basalts (OIB) are thought to originate from partial melting of deep mantle (White 2010), and therefore providing information on deep mantle's composition, evolution, and the interaction between the mantle and the surface layers (Hofmann 1997).

The isotope compositions of Sr, Nd, Pb, Hf, Os, H, O, S, Si, Mg, Ca, and trace elements have been used to study the origins and evolutions of OIB (Cabral et al. 2013; Delavault et al. 2016; Hofmann 2014; Huang et al. 2011; Loewen et al. 2019; Pringle et al. 2016; Wang et al. 2003, 2016). These studies have concluded that subducted oceanic crust, in addition to primitive mantle, has contributed materials to OIB's mantle source. However, the observed variation of Sr, Nd, Pb, Hf isotopes and trace elements can be alternatively explained by the variation of oceanic lithosphere thickness (Niu et al. 2011). Isotope fractionations during subduction (John et al. 2012), partial melting (Wang et al. 2016; Zhu et al. 2018), and fractional crystallization (Wang et al. 2003) cannot be unambiguously ruled out for the observed variation of stable isotopes.

To understand subducted oceanic crust's role in OIB's origin, it is important to quantify its fraction at the mantle source (Sobolev et al. 2007). Although sulfur mass-independent fractionation (S-MIF) found in Mangaia and

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Pitcairn islands show that oceanic sediments can survive in subducted oceanic crust (Cabral et al. 2013; Delavault et al. 2016), it cannot be used to determine its exact fraction in OIB's mantle source owing to large variation of sulfur isotope compositions in subducted oceanic crust (Farquhar et al. 2000). In addition, S-MIF signature is only useful for subducted oceanic crusts around or before the great oxidation event (Farquhar et al. 2000).

In this study, we propose that the triple oxygen isotope compositions ($\Delta^{17}O$) in olivine are exempted from these uncertainties and can serve as a unique tool to resolve OIB's origin. Here $\Delta^{17}O \equiv \delta^{17}O' - 0.5305 \times \delta^{18}O'$ (ref. Bao et al. 2016; Pack and Herwartz 2014), $\delta^x O' = \ln(1 + \delta^x O)$, $\delta^x O = {}^xR/R_{ref} - 1$, ${}^xR = {}^xO/{}^{16}O$, *ref* is the reference material for oxygen isotope measurements, and *x* is 17 or 18. Our working hypothesis is that high-temperature processes (e.g. > 1000 °C) cannot shift olivine's $\Delta^{17}O$ away from that of primitive mantle, but the addition of subducted oceanic crust to OIB's mantle source will because subducted oceanic sediments and hydrothermally altered oceanic crust have respectively negative and positive $\Delta^{17}O$ values, relative to that of the primitive mantle, due to their interactions with ocean water (Pack and Herwartz 2014; Sengupta and Pack 2018; Sharp et al. 2018) (Fig. 1). We will test this hypothesis by (1) theoretically calculating triple oxygen isotope relationships for related olivine-mineral pairs (i.e. the θ values), with a special interest in high temperatures relevant to olivine formation; and (2) examining published $\Delta^{17}O$ values in OIB's olivine sampled worldwide.

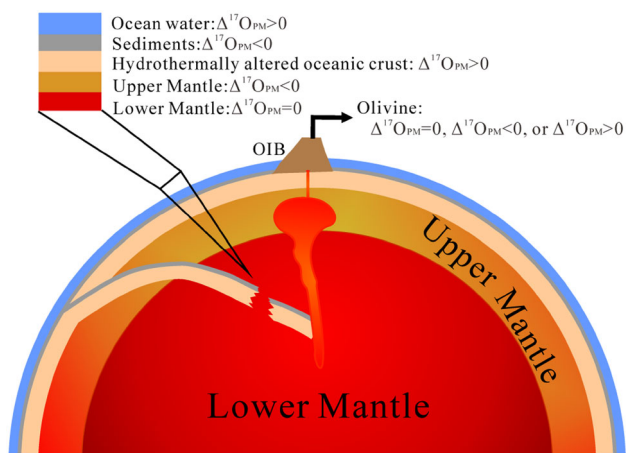


Fig. 1 A cartoon depicting the rationale of our hypothesis. The $\Delta^{17}O$ values presented in this figure are relative to the primitive mantle value

2 Methods

Density functional theory has been used to estimate the oxygen isotope fractionation factor ${}^{18}\alpha$ among different silicate minerals (Meheut et al. 2009; Qin et al. 2016). Forsterite, clinoenstatite, diopside, enstatite, spinel, and pyrope are selected as mineral representatives of the mantle (McDonough and Rudnick 1998). Although other minerals, e.g. ilmenite and magnetite, may be involved in basalt melt evolution, they are not considered here due to their accessory nature. Volatile components, e.g. H_2O , CO_2 , and SO_2 , are not discussed here either, because their role in changing the oxygen isotope compositions of basalt melts is limited (e.g. < 0.3‰) (Eiler 2001).

Starkey et al. (2016) presented a systematic investigation of $\Delta^{17}O$ in olivine samples, and Greenwood et al. (2018) recalibrated their original data and presented additional measurement details. We therefore focus on the $\Delta^{17}O$ data documented in Greenwood et al.'s paper.

2.1 Density functional theory (DFT) calculations

The equilibrium triple oxygen isotope relationship θ between two different minerals can be calculated by Cao and Liu (2011) and Hayles et al. (2018):

$$\theta_{a-b}^E = \kappa_a - \kappa_b \times \frac{\ln {}^{18}\beta_b}{\ln {}^{18}\alpha_{a-b}} \quad (1)$$

where $\kappa \equiv \ln {}^{17}\beta / \ln {}^{18}\beta$, ${}^{18}\alpha_{a-b} \equiv {}^{18}\beta_a / {}^{18}\beta_b$, β is the equilibrium isotope fractionation between the mineral in question and the oxygen atom in ideal gas state, ${}^{18}\alpha_{a-b}$ is the equilibrium isotope fractionation between 'a' and 'b', and 'a' and 'b' refer to two different minerals.

The β values can be estimated by partition function ratios. Taking ${}^{18}\beta$ for olivine as an example, there are 4 oxygen sites in one silica tetrahedral structure unit, and each of them corresponds to a partition function ratio, then,

$${}^{18}\beta_{ol} = \frac{({}^{18}O/{}^{16}O)_{ol}}{({}^{18}O/{}^{16}O)_o} = \frac{1}{4} \sum_{i=1}^4 f(Si^{16}O_3^{18}O^i) \quad (2)$$

where $f(Si^{16}O_3^{18}O^i)$ is the partition function ratio of $Si^{16}O_3^{18}O^i$ to $Si^{16}O_4$, and 'i' refers to the *i*th site. The partition function ratio can be calculated by Bigeleisen and Mayer (1947) and Urey (1947),

$$f(Si^{16}O_3^{18}O^i) = \prod_j \frac{u_j^* e^{-u_j^*/2}}{u_j e^{-u_j/2}} \frac{1 - e^{-u_j}}{1 - e^{-u_j^*}} \quad (3)$$

where *N* is the number of atoms in the unit cell for olivine; u_j is equal to $hc\omega_j/k_bT$, in which *h* is the Planck constant, *c* the speed of light, ω_j the *j*th normal vibration mode, k_b the Boltzmann constant, and *T* temperature in Kelvin. The terms with star (*) refer to the isotopologues $Si^{16}O_3^{18}O^i$.

The vibrational frequencies for each mineral were calculated within DFT, and the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional (Perdew et al. 1996) was employed. The projector augmented wave (PAW) pseudopotentials were used for all elements with a cut off energy of 600 eV. Brillouin-zone integrations were done on a grid of $3 \times 3 \times 3$ k-point centered at Gamma. The unit cell was used for structure optimization, and then the unit cell or super cell was constructed for vibrational frequency calculation. The Hessian matrix was determined by density functional perturbation theory (DFPT) at the Gamma point. All DFT calculations were carried out by Vienna Ab initio Simulation Package (VASP) (Kresse and Furthmüller 1996).

2.2 Recalibrating published $\Delta^{17}O$ data to the primitive mantle scale

In this study, olivine samples with high $^3\text{He}/^4\text{He}$ ratio from Ofu Island were chosen as the representative of the $\Delta^{17}O$ in the primitive mantle, since the mantle source of these olivine samples has shown no contamination from crust materials (Jackson et al. 2007). Although Ofu lava may not result from primitive chondritic materials directly, its $\Delta^{17}O$ will equal to that of the primitive mantle as long as no crust contamination has been added to its mantle source, because differentiation at high temperatures does not change the $\Delta^{17}O$ (See Sect. 4).

Once this was done, we used their averaged $\delta^{17}O$ and $\delta^{18}O$ to recalibrate the published data. The original data can be found in Greenwood et al. (2018), and the corresponding $\delta^{17}O_r$, $\delta^{18}O_r$, and $\Delta^{17}O_{PM}$ were calculated by

$$\delta^x O_r = 1000 \times \ln \left(\frac{\delta^x O_o + 1000}{\delta^x O_{ofu-avg} + 1000} \right) \quad (4a)$$

$$\Delta^{17}O_{PM} = \delta^{17}O_r - 0.5305 \times \delta^{18}O_r \quad (4b)$$

where $\delta^x O_r$ and $\delta^x O_o$ represent the recalibrated and original δ values for the corresponding measurements, respectively; $\delta^x O_{ofu-avg}$ refers to the averaged δ values for a set of olivine samples with high $^3\text{He}/^4\text{He}$ ratio from Ofu Island; ‘x’ refers to 17 or 18; the subscript ‘PM’ in $\Delta^{17}O_{PM}$ refer to a $\Delta^{17}O$ value with respect to that of the primitive mantle.

3 Results

The calculated θ values were presented in Fig. 2 and Table S1, and the recalibrated $\Delta^{17}O_{PM}$ values were given in Fig. 3 and Table S2. These results show that the equilibrium θ values for the related mineral pairs range from 0.5300 to 0.5303 at temperatures from 1000 °C to 1300 °C

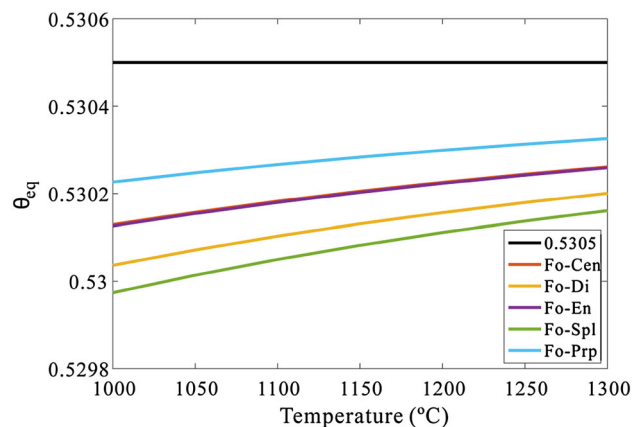


Fig. 2 Calculated equilibrium triple oxygen isotope relationships θ_{eq} for different olivine-mineral pairs at different temperatures above 1000 °C. The 0.5305 line is our reference line. The largest difference between the calculated θ_{eq} and 0.5305 is 0.0005, which corresponds to a variation of less than 0.5 ppm in the $\Delta^{17}O_{PM}$ at this temperature range. Fo, Cen, Di, En, Spl, and Prp refer to Forsterite, Clinoenstatite, Diopside, Enstatite, Spinel, and Pyrope, respectively

(Fig. 2), and the recalibrated $\Delta^{17}O_{PM}$ values for published olivine data range from -13.8 ppm to 15.0 ppm (Fig. 3). The observed variation of $\Delta^{17}O_{PM}$ will be explored below.

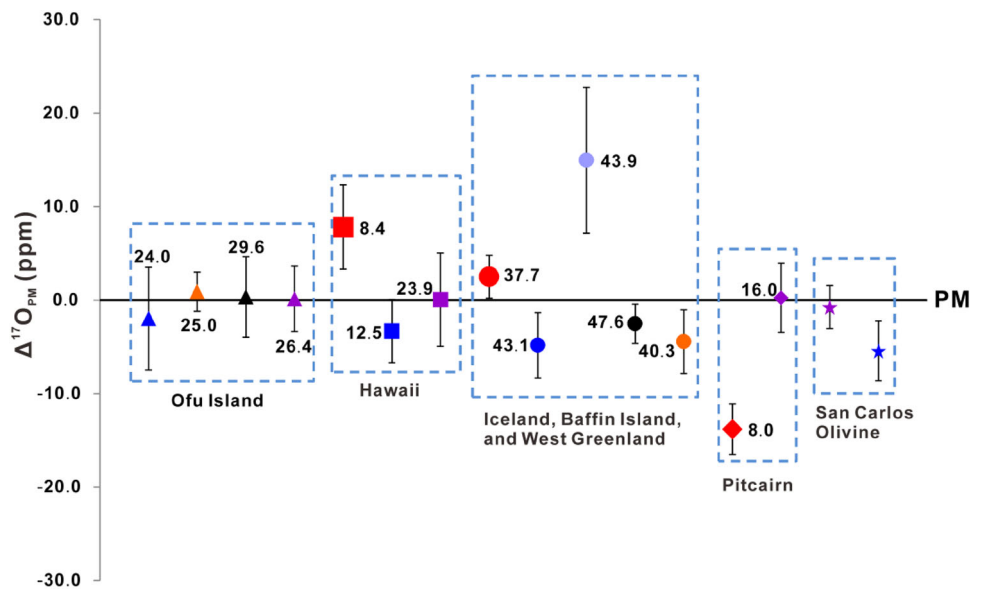
4 Discussion

4.1 Partial melting and fractional crystallization cannot fractionate $\Delta^{17}O_{PM}$ values measurably in olivine

The largest vibrational frequency for these mantle related minerals is about 1100 cm^{-1} (ref. Lin 2004), which corresponds to a u value ($\equiv hc\omega_j/k_bT$) less than 1.24 at 1000 °C and above. High temperature approximation for isotope effect calculation is applicable in this case (Bigeleisen and Mayer 1947). Therefore, the equilibrium θ values should be close to their high temperature limit, i.e. 0.5305 (Cao and Liu 2011; Young et al. 2002). Our calculated θ values are consistent with this theoretical estimation.

It is known that the pressure can affect the ^{18}O isotope fractionation (Polyakov and Kharlashina 1994). However, the influence of pressure on the θ value is expected to be small. For example, although the largest vibrational frequency for forsterite can increase from 960 cm^{-1} at 0 GPa to 1180 cm^{-1} at 50 GPa (Durben et al. 1993), the corresponding increase of u value is less than 0.25 at 1000 °C and above. Therefore, the increase of pressure does not affect the applicability of high temperature approximation for isotope effect calculation at these high temperatures (Bigeleisen and Mayer 1947).

Fig. 3 Recalibrated $\Delta^{17}O_{PM}$ value and $^3\text{He}/^4\text{He}$ ratio (number close to the data symbol) for olivine samples separated from basalts from different locations. All $^3\text{He}/^4\text{He}$ ratios are reported relative to the atmospheric one (i.e. R/R_a). The error bar is given by $1 \times \text{SEM}$ (i.e. one standard error of the mean). The original oxygen isotope data are from reference (Greenwood et al. 2018) and the original $^3\text{He}/^4\text{He}$ ratios from references (Ellam and Stuart 2004; Garapić et al. 2015; Jackson et al. 2007; Kurz et al. 2004; Starkey et al. 2009). Different colors represent different olivine samples as detailed in Table S2



Anharmonic correction can also influence oxygen isotope fractionation, its contribution to the equilibrium θ is expected to be small (Cao and Liu 2011; Hayles et al. 2017). The nuclear volume effect and the Diagonal Born–Oppenheimer Correction are also estimated to be negligible for oxygen isotopes at these high temperatures following established approaches (Yang and Liu 2015; Zhang and Liu 2018).

In addition, our calculated θ values are consistent with field observations (Pack et al. 2016). Therefore, the values of θ for partial melting and fractional crystallization processes associated with olivine formation are estimated to be about 0.5302 ± 0.0001 .

Given the limited ^{18}O isotope fractionation associated with partial melting and fractional crystallization (i.e. around 1‰ or less) (Eiler 2001), the above range of θ values can only contribute to a change in the $\Delta^{17}O_{PM}$ of less than 0.5 ppm. Therefore, partial melting and fractional crystallization processes cannot fractionate $\Delta^{17}O_{PM}$ measurably.

4.2 The observed small $\Delta^{17}O_{PM}$ variation is real

The observed variation of $\Delta^{17}O_{PM}$ is small (Fig. 3). Most of the data are even smaller than their one standard deviation (Table S2). However, we think this small variation is real due to the reasons given below.

4.2.1 Reduce the errors through careful recalibration

It is aware that accurate mineral $\Delta^{17}O$ values are difficult to determine to the ppm level in VSMOW scale (Pack et al. 2016). The $\Delta^{17}O$ could differ by up to 50 ppm even for the same mineral measured in the same laboratory (Pack et al.

2016). The reason for this variability is due to the difficulty in measuring a mineral and VSMOW in the same laboratory (Pack et al. 2016). Fortunately, this type of error can be avoided if all $\Delta^{17}O$ values are reported directly relative to olivine mineral instead of VSMOW. This is the reason why we recalibrated the original $\Delta^{17}O$ values to primitive mantle scale instead of VSMOW scale.

Even a mineral and VSMOW can be measured in the same laboratory, different laboratories may obtain different $\Delta^{17}O$ values for a mineral relative to VSMOW (Pack et al. 2016; Sharp et al. 2016), which might be caused by the pressure baselines effect (Yeung et al. 2018). Therefore, only data measured in the same laboratory, i.e. the ones from the Open University (Greenwood et al. 2018), are used in this study. The systematic errors can be largely reduced in this way.

When recalibrating, we chose 0.5305 for the reference line instead of 0.5262 used by the original paper (Greenwood et al. 2018), since the triple isotope relationship should be around 0.5302 during olivine formation as discussed above. This is critical when studying small variation of the $\Delta^{17}O_{PM}$, especially for samples with large $\delta^{18}\text{O}$ difference relative to the primitive mantle.

After a careful recalibration procedure, the errors associated with different laboratories, reference difference (i.e. primitive mantle vs. VSMOW), and difference of olivine formation process can be reduced. However, this procedure cannot exclude the role of statistic bias in the small $\Delta^{17}O_{PM}$ variation presented in Fig. 3 because some of the olivine samples are only measured 2 or 3 times (Greenwood et al. 2018). More $\Delta^{17}O_{PM}$ measurements are required to rule out this potential error. Instead, here the $^3\text{He}/^4\text{He}$ ratios in these olivine samples are used to examine the influence of statistic bias.

4.2.2 The $^3\text{He}/^4\text{He}$ ratio in olivine samples

If the small variation of $\Delta^{17}O_{PM}$ is the result of poor statistics, the values of $\Delta^{17}O_{PM}$ in those olivine samples from the same location should not be expected to correlate to their $^3\text{He}/^4\text{He}$ ratios. However, as shown in Fig. 3, an olivine sample with a higher $^3\text{He}/^4\text{He}$ ratio tends to have a $\Delta^{17}O_{PM}$ value closer to zero, in contrast to other olivine samples within the same location. Note that there is no $^3\text{He}/^4\text{He}$ data for San Carlos olivine. Given that these $^3\text{He}/^4\text{He}$ ratios are measured by different and independent groups, this correlation should not be caused by statistic bias. In fact, this correlation is expected, as will be discussed below.

Therefore, even though the statistical errors are large, the observed small variations of $\Delta^{17}O_{PM}$ values are probably real.

4.3 Subducted oceanic crusts cause the small $\Delta^{17}O_{PM}$ variation in olivine samples

Several mechanisms can cause the small $\Delta^{17}O_{PM}$ variation among olivine samples. One possibility is that the primitive mantle is heterogeneous in the $\Delta^{17}O_{PM}$. If this is the case, the olivine samples from different locations and origins are not expected to have the same $\Delta^{17}O_{PM}$, i.e. $\Delta^{17}O_{PM} = 0$, even they have relatively high $^3\text{He}/^4\text{He}$ ratios. However, this possibility is inconsistent with the results presented in Fig. 3. In addition, the values of $\Delta^{17}O_{PM}$ in basalts from the Amsterdam-St. Paul plateau and Gulf of Tadjoura are also equal to zero within the error (see Table S1), which is consistent with previous suggestion that primitive mantle has contributed materials to the mantle sources of basalts in these two regions (Dosso et al. 1988; Marty et al. 1993). Therefore, heterogeneity of primitive mantle may be true for some elements or isotopes, but not for the $\Delta^{17}O_{PM}$ of primitive mantle.

Mantle derived olivine formed at high temperatures (e.g. 1200 ± 100 °C) (Mattey et al. 1994). Fresh olivine can hardly survive once it interacts with water due to serpentinization. Therefore, the common isotope alteration mechanism, i.e. fluid-rock interaction, is not a plausible mechanism for the observed $\Delta^{17}O_{PM}$ variations among olivine samples.

Now let us examine the role of subducted oceanic crust and see if the observed variations of the $\Delta^{17}O_{PM}$ in olivine samples can be accounted for by a simple mixing. To explain the negative $\Delta^{17}O_{PM}$ values in olivine samples from Pitcairn Island (i.e. the red diamond in Fig. 3), subducted oceanic sediments had to be mixed in, while the assimilation of the modern ocean sediments is not likely. Here ‘assimilation’ refers to the interaction between magma and its conduit wall materials in the crust, being

distinct from the mixed-in from the ‘subducted’ crustal materials. This conclusion is consistent with the observed S-MIF and Mg isotope signatures in basalt samples from Pitcairn (Delavault et al. 2016; Wang et al. 2018). Moreover, the addition of subducted oceanic crust to primitive mantle can lower the $^3\text{He}/^4\text{He}$ ratio, which is consistent with the results presented in Fig. 3.

Similarly, the olivine samples from Mauna Loa and Iceland (i.e. the red square and circle in Fig. 3), which possess small positive $\Delta^{17}O_{PM}$ values, should carry signatures of hydrothermally altered oceanic crusts. Although the $\Delta^{17}O_{PM}$ values alone cannot distinguish the subducted crust from the crust assimilation, previous studies on lavas from Mauna Loa (Pietruszka et al. 2013) and Iceland (Kokfelt et al. 2006) suggested that subducted hydrothermally altered oceanic crusts involved in the formation of these basalts. The small positive $\Delta^{17}O_{PM}$ shifts is consistent with these previous studies.

Olivine samples from Baffin Island, West Greenland, and San Carlos are all associated with basalts being erupted into continental crusts. The $\Delta^{17}O_{PM}$ value of continental crust is normally negative (Sengupta and Pack 2018), while it can reach as positive as 90 ppm when the continental crust has interacted with meteoric water (Herwartz et al. 2015). Therefore, the non-zero $\Delta^{17}O_{PM}$ values in these olivine samples can be caused either by the addition of subducted oceanic crust or by the assimilation of continental crust. The $\Delta^{17}O_{PM}$ value alone cannot separate the two different mechanisms, and we will not discuss these non-zero $\Delta^{17}O_{PM}$ values further here.

4.4 Estimate the fraction of subducted oceanic crust in OIB’s mantle source using the observed $\Delta^{17}O_{PM}$ values

As discussed above, the small $\Delta^{17}O_{PM}$ variation in olivine samples from Pitcairn, Mauna Loa, and Iceland can be explained by the mixing between the subducted oceanic crust and the primitive mantle. To estimate the fraction of subducted oceanic crust in OIB’s mantle source, the oxygen isotope compositions for the related two reservoirs have to be determined first. For primitive mantle, its $\Delta^{17}O_{PM}$ value is 0.0 ppm as defined here. For subducted ocean sediments, there are two potential representatives we can choose. One is the shales (Bindeman et al. 2018; Sengupta and Pack 2018) and the other is siliceous sediments (Pack and Herwartz 2014; Sengupta and Pack 2018). Here we use shales because their average $\delta^{18}\text{O}$ value is close to that of the top section of the subducting slab (Bindeman et al. 2018; Gregory and Taylor 1981). If this is the case, the $\Delta^{17}O_{PM}$ value of subducted oceanic sediments is -132.7 ppm (see Table S2). Then the fraction of ocean sediments in the mantle sources of Pitcairn (i.e. the one

with negative $\Delta^{17}O_{PM}$ lavas is estimated to be $10.4 \pm 2.0\%$ [i.e. $(-13.8 \pm 2.7)/(-132.7)$] (Fig. 4). This estimation will not be accurate if the related two reservoirs have a large $\delta^{18}O$ difference due to the non-linear mixing nature of the $\Delta^{17}O$ (Herwartz et al. 2015). The fraction is then re-calculated to be 10.3% when the non-linear mixing nature of the $\Delta^{17}O$ is included, and the result is identical to the one determined by $\Delta^{17}O_{PM}$ only within the error. Therefore, the fraction determined by $\Delta^{17}O_{PM}$ is good enough, and only the value of $\Delta^{17}O_{PM}$ will be used to estimate the contribution of hydrothermally altered oceanic crust below.

The $\Delta^{17}O_{PM}$ value for subducted hydrothermally altered oceanic crust was estimated to be 35.0 ppm (Sengupta and Pack 2018), which constrains the fractions of subducted hydrothermally altered oceanic crust in the mantle sources of Mauna Loa and Iceland lavas to be $22.3 \pm 12.9\%$ and $7.1 \pm 6.6\%$ [i.e. $(7.8 \pm 4.5)/35$ and $(2.5 \pm 2.3)/35$], respectively. Our determined fractions of hydrothermally altered oceanic crust for Mauna Loa and Iceland lavas are close to the previous estimates using trace elements (Pietruszka et al. 2013; Sobolev et al. 2007; Wang et al. 2010).

Note that the $\delta^{18}O$ alone can also be used to constrain OIB's origin (Eiler 2001). However, $\delta^{18}O$ -based interpretation has extra degrees of freedom. This is because the $\delta^{18}O$ value is not only dependent on the mixing between the subducted oceanic crust and primitive mantle but also on the ^{18}O isotope fractionation during degassing, partial melting, and fractional crystallization (Eiler 2001). For example, the $\delta^{18}O$ value in olivine from Mauna Loa is expected to be low due to the addition of subducted hydrothermally altered oceanic crust to its mantle source, but it is not in reality (see Table S2). The ^{18}O isotope fractionation should have played a role, and additional geochemical parameters might be helpful to reconcile this inconsistency.

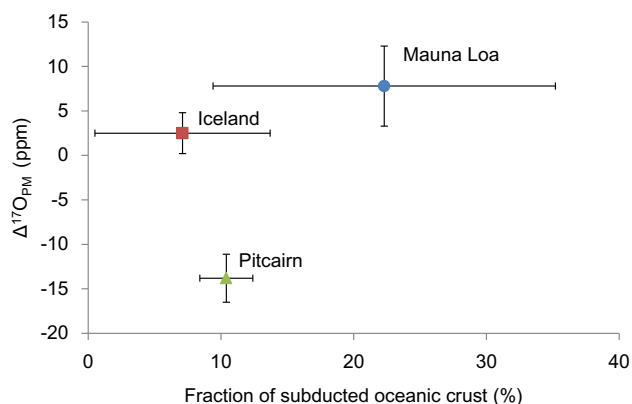


Fig. 4 The estimated fractions of the subducted oceanic crust in OIB's mantle source. The error bar is determined by $1 \times \text{SEM}$ value of $\Delta^{17}O_{PM}$

4.5 Subducted oceanic crusts might only exist locally in the mantle plume

The olivine samples from Hawaii plume can also have zero $\Delta^{17}O_{PM}$ values (See Fig. 3). There are three possible mechanisms to interpret these zero $\Delta^{17}O_{PM}$ values. The first is that the subducted hydrothermally altered oceanic crust exists locally and does not affect their entire mantle source. The second one is that subducted oceanic crust does exist in their mantle source, but this crust barely experiences hydrothermal alterations. The third one is that the $\Delta^{17}O_{PM}$ value of part of the subducted oceanic crust is altered to be zero during subduction process. If the last two cases were true, the $^3\text{He}/^4\text{He}$ values in these olivine samples should have been low, which does not agree with the observation (see Fig. 3). Furthermore, oxygen is a major element in the subducting slab and the amount of fluid derived from the slab is relatively small, and subduction process is thus not expected to change the $\Delta^{17}O_{PM}$ substantially in the subducted oceanic crust. Therefore, the first mechanism is the most likely scenario to interpret the zero $\Delta^{17}O_{PM}$ values in these olivine samples. In other words, subducted oceanic crust only exists locally in the mantle plume and is not always sampled by the OIBs. This conclusion is consistent with earlier studies on Hawaii plume mantle source (Pietruszka et al. 2013; Wang et al. 2010). Local mantle chemical heterogeneity is also supported by the $\Delta^{17}O_{PM}$ results determined for the olivine samples from Pitcairn (See Fig. 3). Considering the observed S-MIF in Pitcairn basalts (Delavault et al. 2016), the $\Delta^{17}O$ heterogeneity generated by subducted oceanic crust can be preserved locally in deep mantle for billions of years.

5 Concluding remarks

The large compositional variation observed in OIBs is generally attributed to the recycling of oceanic crust into the deep mantle. Our analysis of the $\Delta^{17}O_{PM}$ values of olivine from different locations suggests that there had existed a $\Delta^{17}O$ -homogeneous deep mantle, but the recycling of oceanic crusts has since generated $\Delta^{17}O$ heterogeneities in mantle. Those $\Delta^{17}O$ -heterogeneous regions are likely to be limited spatially. With the addition of $\Delta^{17}O_{PM}$ values of olivine, partition of trace elements, stable isotope fractionation, and variation of radiogenic isotopes can be better quantified. This study calls for an effort to improve high-precision $\Delta^{17}O$ analysis of terrestrial minerals.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interests.

References

- Bao H, Cao X, Hayles JA (2016) Triple oxygen isotopes: fundamental relationships and applications. *Annu Rev Earth Planet Sci* 44:463–492
- Bigeleisen J, Mayer MG (1947) Calculation of equilibrium constants for isotopic exchange reactions. *J Chem Phys* 15:261–267
- Bindeman IN, Zakharov DO, Palandri J, Greber ND, Dauphas N, Retallack GJ, Hofmann A, Lackey JS, Bekker A (2018) Rapid emergence of subaerial landmasses and onset of a modern hydrologic cycle 2.5 billion years ago. *Nature* 557:545–548
- Cabral RA, Jackson MG, Rose-Koga EF, Koga KT, Whitehouse MJ, Antonelli MA, Farquhar J, Day JMD, Hauri EH (2013) Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of Archaean crust. *Nature* 496:496–500
- Cao X, Liu Y (2011) Equilibrium mass-dependent fractionation relationships for triple oxygen isotopes. *Geochim Cosmochim Acta* 75:7435–7445
- Delavault H, Chauvel C, Thomassot E, Devey CW, Dazas B (2016) Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume. *Proc Natl Acad Sci USA* 113:12952–12957
- Dosso L, Bougault H, Beuzart P, Calvez J-Y, Joron J-L (1988) The geochemical structure of the South-East Indian Ridge. *Earth Planet Sci Lett* 88:47–59
- Durben DJ, McMillan PF, Wolf GH (1993) Raman-study of the high-pressure behavior of forsterite (Mg_2SiO_4) crystal and glass. *Am Mineral* 78:1143–1148
- Eiler JM (2001) Oxygen isotope variations of basaltic lavas and upper mantle rocks. *Rev Mineral Geochem* 43:319–364
- Ellam RM, Stuart FM (2004) Coherent He–Nd–Sr isotope trends in high $^3\text{He}/^4\text{He}$ basalts: implications for a common reservoir, mantle heterogeneity and convection. *Earth Planet Sci Lett* 228:511–523
- Farquhar J, Bao HM, Thiemens M (2000) Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289:756–758
- Garapic G, Jackson MG, Hauri EH, Hart SR, Farley KA, Blusztajn JS, Woodhead JD (2015) A radiogenic isotopic (He–Sr–Nd–Pb–Os) study of lavas from the Pitcairn hotspot: implications for the origin of EM-1 (enriched mantle 1). *Lithos* 228–229:1–11
- Greenwood RC, Barrat J-A, Miller MF, Anand M, Dauphas N, Franchi IA, Sillard P, Starkey NA (2018) Oxygen isotopic evidence for accretion of Earth's water before a high-energy Moon-forming giant impact. *Sci Adv* 4:eaa05928
- Gregory RT, Taylor HP (1981) An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail Ophiolite, Oman: evidence for $\delta^{18}\text{O}$ buffering of the oceans by deep (> 5 km) seawater-hydrothermal circulation at mid-ocean ridges. *J Geophys Res* 86:2737–2755
- Hayles JA, Cao X, Bao H (2017) The statistical mechanical basis of the triple isotope fractionation relationship. *Geochem Perspect Lett* 3:1–11
- Hayles J, Gao C, Cao X, Liu Y, Bao H (2018) Theoretical calibration of the triple oxygen isotope thermometer. *Geochim Cosmochim Acta* 235:237–245
- Herwartz D, Pack A, Krylov D, Xiao Y, Muehlenbachs K, Sengupta S, Di Rocco T (2015) Revealing the climate of snowball Earth from $\Delta^{17}\text{O}$ systematics of hydrothermal rocks. *Proc Natl Acad Sci USA* 112:5337–5341
- Hofmann AW (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet Sci Lett* 90:297–314
- Hofmann AW (1997) Mantle geochemistry: the message from oceanic volcanism. *Nature* 385:219
- Hofmann AW (2014) Sampling mantle heterogeneity through oceanic basalts: Isotopes and trace elements. In: Holland HD, Turekian KK (eds) *Treatise on geochemistry*, 2nd edn. Elsevier, Oxford, pp 67–101
- Huang S, Farkaš J, Jacobsen SB (2011) Stable calcium isotopic compositions of Hawaiian shield lavas: evidence for recycling of ancient marine carbonates into the mantle. *Geochim Cosmochim Acta* 75:4987–4997
- Jackson MG, Kurz MD, Hart SR, Workman RK (2007) New Samoan lavas from Ofu Island reveal a hemispherically heterogeneous high $^3\text{He}/^4\text{He}$ mantle. *Earth Planet Sci Lett* 264:360–374
- John T, Gussone N, Podladchikov YY, Bebout GE, Dohmen R, Halama R, Klemd R, Magna T, Seitz H-M (2012) Volcanic arcs fed by rapid pulsed fluid flow through subducting slabs. *Nat Geosci* 5:489
- Kokfelt TF, Hoernle KAJ, Hauff F, Fiebig J, Werner R, Garbe-SchÖnberg D (2006) Combined trace element and Pb–Nd–Sr–O isotope evidence for recycled oceanic crust (upper and lower) in the Iceland mantle plume. *J Petrol* 47:1705–1749
- Kresse G, Furthmüller J (1996) Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B* 54:11169–11186
- Kurz MD, Curtice J, Lott DE, Solow A (2004) Rapid helium isotopic variability in Mauna Kea shield lavas from the Hawaiian Scientific Drilling Project. *Geochem Geophys Geosyst* 5:Q04G14
- Lin C-C (2004) Pressure-induced polymorphism in enstatite (MgSiO_3) at room temperature: clinoenstatite and orthoenstatite. *J Phys Chem Solids* 65:913–921
- Loewen MW, Graham DW, Bindeman IN, Lupton JE, Garcia MO (2019) Hydrogen isotopes in high $^3\text{He}/^4\text{He}$ submarine basalts: primordial vs. recycled water and the veil of mantle enrichment. *Earth Planet Sci Lett* 508:62–73
- Marty B, Appora I, Barrat J-AA, Deniel C, Vellutini P, Vidal P (1993) He, Ar, Sr, Nd and Pb isotopes in volcanic rocks from Afar: evidence for a primitive mantle component and constraints on magmatic sources. *Geochem J* 27:219–228
- Mattey D, Lowry D, Macpherson C (1994) Oxygen isotope composition of mantle peridotite. *Earth Planet Sci Lett* 128:231–241
- McDonough WF, Rudnick RL (1998) Mineralogy and composition of the upper mantle. *Rev Mineral Geochem* 37:139–164
- Meheut M, Lazzeri M, Balan E, Mauri F (2009) Structural control over equilibrium silicon and oxygen isotopic fractionation: a first-principles density-functional theory study. *Chem Geol* 258:28–37
- Niu YL, Wilson M, Humphreys ER, O'Hara MJ (2011) The origin of intra-plate ocean island basalts (OIB): the lid effect and its geodynamic implications. *J Petrol* 52:1443–1468
- Pack A, Herwartz D (2014) The triple oxygen isotope composition of the Earth mantle and understanding variations in terrestrial rocks and minerals. *Earth Planet Sci Lett* 390:138–145
- Pack A, Tanaka R, Hering M, Sengupta S, Peters S, Nakamura E (2016) The oxygen isotope composition of San Carlos olivine on the VSMOW2-SLAP2 scale. *Rapid Commun Mass Spectrom* 30:1495–1504
- Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. *Phys Rev Lett* 77:3865–3868

- Pietruszka AJ, Norman MD, Garcia MO, Marske JP, Burns DH (2013) Chemical heterogeneity in the Hawaiian mantle plume from the alteration and dehydration of recycled oceanic crust. *Earth Planet Sci Lett* 361:298–309
- Polyakov VB, Kharlashina NN (1994) Effect of pressure on equilibrium isotopic fractionation. *Geochim Cosmochim Acta* 58:4739–4750
- Pringle EA, Moynier F, Savage PS, Jackson MG, Moreira M, Day JMD (2016) Silicon isotopes reveal recycled altered oceanic crust in the mantle sources of Ocean Island Basalts. *Geochim Cosmochim Acta* 189:282–295
- Qin T, Wu F, Wu Z, Huang F (2016) First-principles calculations of equilibrium fractionation of O and Si isotopes in quartz, albite, anorthite, and zircon. *Contrib Mineral Petrol* 171:91
- Sengupta S, Pack A (2018) Triple oxygen isotope mass balance for the Earth's oceans with application to Archean cherts. *Chem Geol* 495:18–26
- Sharp ZD, Gibbons JA, Maltsev O, Atudorei V, Pack A, Sengupta S, Shock EL, Knauth LP (2016) A calibration of the triple oxygen isotope fractionation in the SiO₂–H₂O system and applications to natural samples. *Geochim Cosmochim Acta* 186:105–119
- Sharp ZD, Wostbrock JAG, Pack A (2018) Mass-dependent triple oxygen isotope variations in terrestrial materials. *Geochem Perspect Lett* 7:27–31
- Sobolev AV, Hofmann AW, Kuzmin DV, Yaxley GM, Arndt NT, Chung S-L, Danyushevsky LV, Elliott T, Frey FA, Garcia MO, Gurenko AA, Kamenetsky VS, Kerr AC, Krivolutskaya NA, Matvienkov VV, Nikogosian IK, Rocholl A, Sigurdsson IA, Sushchevskaya NM, Teklay M (2007) The amount of recycled crust in sources of mantle-derived melts. *Science* 316:412
- Starkey NA, Stuart FM, Ellam RM, Fitton JG, Basu S, Larsen LM (2009) Helium isotopes in early Iceland plume picrites: constraints on the composition of high ³He/⁴He mantle. *Earth Planet Sci Lett* 277:91–100
- Starkey NA, Jackson CRM, Greenwood RC, Parman S, Franchi IA, Jackson M, Fitton JG, Stuart FM, Kurz M, Larsen LM (2016) Triple oxygen isotopic composition of the high-³He/⁴He mantle. *Geochim Cosmochim Acta* 176:227–238
- Urey HC (1947) The thermodynamic properties of isotopic substances. *J Chem Soc* 562–581
- Wang Z, Kitchen Nami E, Eiler John M (2003) Oxygen isotope geochemistry of the second HSDP core. *Geochem Geophys Geosyst* 4:8712
- Wang ZR, Eiler JM, Asimow PD, Garcia MO, Takahashi E (2010) Oxygen isotope constraints on the structure and evolution of the Hawaiian plume. *Am J Sci* 310:683–720
- Wang S-J, Teng F-Z, Scott JM (2016) Tracing the origin of continental HIMU-like intraplate volcanism using magnesium isotope systematics. *Geochim Cosmochim Acta* 185:78–87
- Wang X-J, Chen L-H, Hofmann AW, Hanyu T, Kawabata H, Zhong Y, Xie L-W, Shi J-H, Miyazaki T, Hirahara Y, Takahashi T, Senda R, Chang Q, Vaglarov BS, Kimura J-I (2018) Recycled ancient ghost carbonate in the Pitcairn mantle plume. *Proc Natl Acad Sci USA* 115:8682–8687
- White WM (2010) Oceanic island basalts and mantle plumes: the geochemical perspective. *Annu Rev Earth Planet Sci* 38:133–160
- Yang S, Liu Y (2015) Nuclear volume effects in equilibrium stable isotope fractionations of mercury, thallium and lead. *Sci Rep* 5:12626
- Yeung LY, Hayles JA, Hu H, Ash JL, Sun T (2018) Scale distortion from pressure baselines as a source of inaccuracy in triple-isotope measurements. *Rapid Commun Mass Spectrom* 32:1811–1821
- Young ED, Galy A, Nagahara H (2002) Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim Cosmochim Acta* 66:1095–1104
- Zhang Y, Liu Y (2018) The theory of equilibrium isotope fractionations for gaseous molecules under super-cold conditions. *Geochim Cosmochim Acta* 238:123–149
- Zhu H, Liu F, Li X, Wang G, Zhang Z, Sun W (2018) Calcium isotopic compositions of normal Mid-Ocean Ridge Basalts from the Southern Juan de Fuca ridge. *J Geophys Res Solid Earth* 123:1303–1313