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The recycling of marine carbonates and sources of HIMU and FOZO ocean island basalts

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ABSTRACT

Many, and perhaps all, oceanic island basalts (OIB) clearly contain a component of crustal materials that have been returned to the mantle through subduction or other processes. One of the first recycled materials to be identified as a potential source of OIB was mid-ocean ridge basalt (MORB), and this was later fine-tuned as having a long time-integrated (b.y.) high U/Pb ratio or high μ (HIMU) and producing OIB with the most radiogenic Pb isotopic ratios ($^{206}Pb/^{204}Pb > 20$). However, it is becoming more evident that the compositional connection between subducted MORB and HIMU basalts is problematic. As an alternative hypothesis, a small amount (a few %) of recycled Archaean marine carbonates (primarily $CaCO_3$) is proposed to be the main source of the distinct $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ isotopic and major-trace element compositions of classic HIMU and post-Archaean marine carbonates for younger HIMU or the so-called FOZO mantle source. As an extension of the hypothesis, a conceptual model that combines the separate evolutionary histories of ancient oceanic lithosphere, which is the source of OIB, and upper mantle, which is the source of MORB, is also proposed. The model claims that FOZO mainly consists of the lithospheric mantle portion of the ancient metamorphosed oceanic slabs that have accumulated in the deep mantle. Such an ultramafic source is geochemically depleted due to prior extraction of basaltic melt plus removal of the enriched subduction component from the slab through dehydration and metamorphic processes. Combined with other proposed models in the literature, the conceptual model can provide reasonable solutions for the $^{208}Pb/^{204}Pb$, $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, and $^3He/^4He$ isotopic paradoxes or complexities of oceanic lavas. Although these simultaneous solutions for individual paradoxes are qualitative and non-unique, these are unified under a single, marine carbonate recycling hypothesis.

1. Introduction

A number of scientists have proposed that after one or two b.y. of residence, the oceanic crust consisting of mid-ocean ridge basalts (MORB) and overlying sediments that had been subducted into the deep mantle forms a number of discrete mantle source reservoirs, respectively represented by end-members with extreme Sr–Nd–Pb isotopic compositions (Hofmann, 2003; White, 2010; and references therein). The return of subducted oceanic crust as ocean island basalts (OIB) was first proposed through upwelling deep mantle plumes or hotspot volcanism (e.g., Hawkesworth et al., 1979). Although the validity of plume magmatism has recently been questioned (e.g., Foulger et al., 2005 and references therein), OIB as a consequence of crustal recycling remains the consensus. The three end-member OIB sources derived from recycled crust consist of a mantle reservoir with high $^{238}U/^{204}Pb$ ratio (= high μ or HIMU) and geochemically enriched mantle I and II (EMI and EMII, respectively) reservoirs. Recent investigations have clearly shown that EMII originates from recycled continental crust materials (Jackson et al., 2007). On the other hand, HIMU has been proposed to originate from recycled MORB, and there are proposals that EMI most likely comes from recycled pelagic sediments, terrigenous sediments, delaminated continental or oceanic lithosphere, and various combinations thereof (e.g., Chauvel et al., 1992; Hofmann, 2003; White, 2010; and references therein). Together with the proposed geochemically depleted MORB mantle (DMM), HIMU, EMI and EMII represent the mantle end-members in the Sr–Nd–Pb isotopic space (Fig. 1). Although compositionally variable (Stracke et al., 2005), the focal zone (FOZO) inside the isotopic space has also been proposed as an end-member (Hart et al., 1992) and considered by some to be also coming from recycled oceanic crust (e.g., Hanan and Graham, 1996). It also may be a common mantle source to both OIB and MORB (Hanan and Graham, 1996). Moreover, OIB in the FOZO appear to have the highest $^3He/^4He$ ratios (e.g., Hilton et al., 1999) and their compositions are closest to primitive and/or bulk silicate Earth. Thus, some have argued that FOZO comes from the deep, undegassed portion of the mantle (Hanan and Graham, 1996) or a portion of the mantle that has suffered geochemical depletion and long period of isolation (Class and Goldstein, 2005).

The main objective of this paper is to present the marine carbonate recycling hypothesis, which states recycled Archaean carbonates are the key, albeit not sole ingredient, in the source that provides the extremely radiogenic Pb, but unradiogenic $^{87}Sr/^{86}Sr$ isotopic signatures

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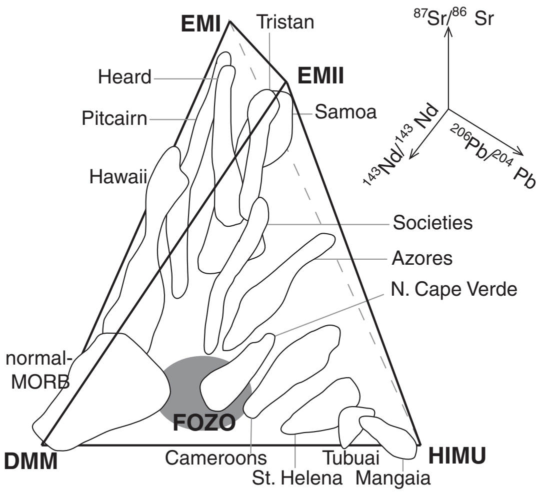

Fig. 1. The mantle Sr–Nd–Pb isotopic tetrahedron showing the proposed mantle end-members (modified from Hauri et al., 1994).

of 'classic' HIMU basalts whereas post-Archaean marine carbonates are the key ingredient in the source that provides the variable HIMU-like Pb isotopic characteristics of the bulk of OIB. The latter are also termed 'young' HIMU or FOZO basalts. Then it describes the extension of the hypothesis — a conceptual model that posits the lithospheric mantle portion of the subduction-processed and metamorphosed oceanic slab now stored in the deeper part of the mantle, perhaps all the way to the core–mantle boundary, is the main source of OIB. This previously subducted ultramafic body comprises the bulk of the ubiquitous FOZO reservoir and produces the basaltic foundation of ocean islands. The proposed distinctive, but less voluminous mantle end-members HIMU, EMI and EMII represent the upper, compositionally variable crustal portion of the subducted oceanic slab. Finally, using the conceptual model, this paper also describes the possible sources of the ^{208}Pb/^{204}Pb, ^{143}Nd/^{144}Nd, ^{176}Hf/^{177}Hf, and ^{3}He/^{4}He signatures in HIMU, the bulk of OIB (or FOZO) and MORB.

2. The source of HIMU

2.1. Current model

The current model for the source of HIMU calls for either a combination of seafloor alteration and/or dehydration of the oceanic slab during subduction that removes Pb but not U from MORB to increase its U/Pb ratio (e.g., Chauvel et al., 1992; Kogiso et al., 1997). Radiogenic decay of U during long residence time (1 to 2 b.y.) in the mantle of eclogite and other high-pressure phase assemblages made from subducted MORB generates the highly radiogenic ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb nature of HIMU. HIMU also has unusually low and limited ^{87}Sr/^{86}Sr for a given ^{143}Nd/^{144}Nd. Thus, its time-integrated U/Pb and Rb/Sr as well as ^{87}Sr/^{86}Sr and ^{206}Pb/^{204}Pb ratios are decoupled, in contrast to other oceanic igneous rocks (Fig. 2a). In this MORB-source model, the low Rb/Sr ratio is also resolved through alteration and subduction dehydration processes that efficiently remove Rb from MORB.

However, some data are inconsistent with the current model. For example, alkali basalt typical of HIMU simply cannot be generated from partial melting of the high-pressure phases of MORB, which are also claimed to be too dense to upwell from the deep mantle (Niu and O'Hara, 2003). In response to this dispute, it has been counter-argued that recycled crust is actually buoyant because it makes up <50% of the upwelling OIB mantle source, with peridotite making up the rest (White, 2010). Alternatively, melts generated from recycled crust can react with peridotite mantle to produce alkalic magma (Mallik and Dasgupta, 2012). Note that because the HIMU source needs high U/Pb and low Rb/Sr ratios in its source, the last two counterarguments require the alteration and subduction dehydration processes to be extremely and selectively efficient in removing only Pb and Rb from the subducted MORB in order to compensate for the low U/Pb and high Rb/Sr ratios of the peridotite comprising >50% of the source. However, such a requirement is most likely unfulfilled as large fractions of U and Sr are also effectively removed from subducted oceanic crust (Kessel et al., 2005; Porter and White, 2009).

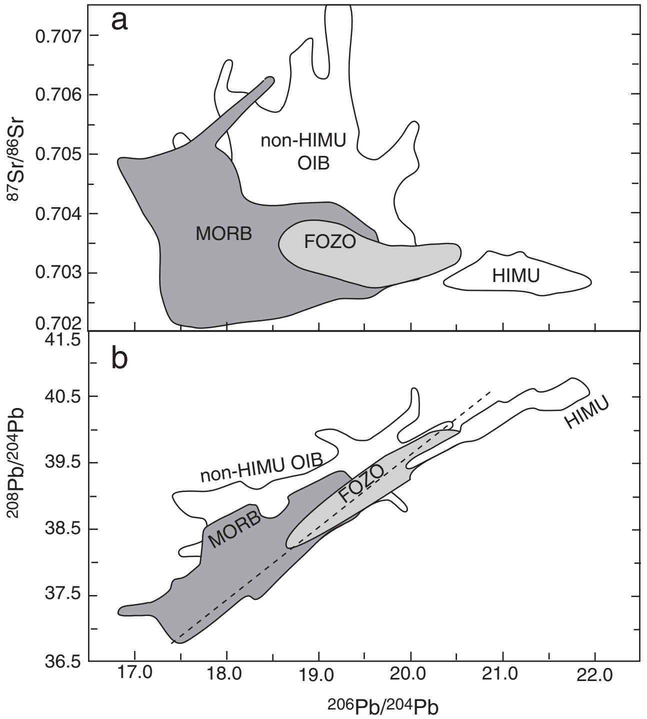

Fig. 2. a. ^{206}Pb/^{204}Pb–^{87}Sr/^{86}Sr and b. ^{206}Pb/^{204}Pb–^{208}Pb/^{204}Pb diagrams for OIB (modified from Stracke et al., 2005). In a., HIMU (Mangaia, Tubuai and St. Helena islands) is distinctly different from other OIB. In b., HIMU is non-linear (indicated by dash line) with FOZO (FOZO's of Hauri et al., 1994 and Stracke et al., 2005; 'C' of Hanan and Graham, 1996) and MORB.

Another contradiction with the MORB-source model is that the 'classic' HIMU islands of St. Helena and Mangaia plus Tubuai of the Cook-Australs chain deviate from and plot below the line defined by MORB and the bulk of OIB with HIMU-like Pb isotopic signature (i.e., with high ^{206}Pb/^{204}Pb ratios but lower than those of HIMU islands) in the ^{208}Pb/^{204}Pb–^{206}Pb/^{204}Pb space (Fig. 2b). Thus, the nonlinear relationship between classic HIMU basalts and the bulk of OIB suggests that the HIMU source must have a history of low time-integrated Th/U ratios, but the high ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios of the former require even higher time-integrated U/Pb and Th/Pb ratios than in the MORB and other OIB sources (Stracke et al., 2005). These islands are hereafter termed HIMU *sensu stricto* whereas the more voluminous HIMU-like islands defining the various FOZO estimates of Hauri et al. (1994) and Stracke et al. (2005) as well as the 'C' component of Hanan and Graham (1996) are termed FOZO. Importantly, a detailed study of the major element composition of OIB by Jackson and Dasgupta (2008) also highlights that St. Helena and Cook-Austral (HIMU) OIB have the lowest SiO_2 and highest CaO/Al_2O_3, FeO^{total} and TiO_2 for given ^{206}Pb/^{204}Pb ratios than other OIB. Interestingly, the same data set of Jackson and Dasgupta (2008) also shows a significant correlation between CaO and ^{206}Pb/^{204}Pb ratio in oceanic lavas, with HIMU having the highest ^{206}Pb/^{204}Pb for a given CaO (Fig. 3a). Moreover, it has lower K_2O and ^{87}Sr/^{86}Sr than EMI and EMII (Fig. 3b).

Compared to HIMU, FOZO as defined above covers a range of composition, but in general has less radiogenic Pb but more radiogenic Sr isotope signatures. It also includes the extension of the (Atlantic and Pacific) MORB and other OIB arrays in the Sr–Pb isotope ratio diagram

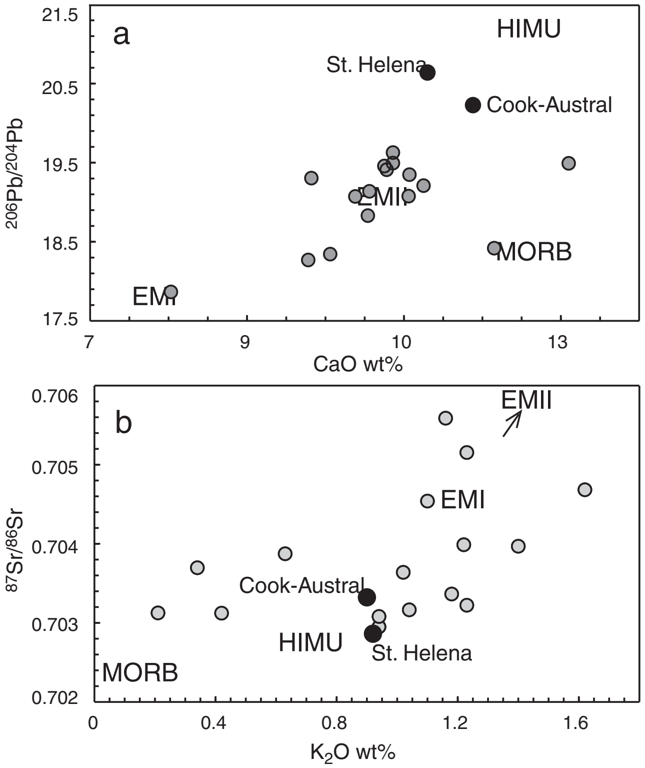

Fig. 3. a. ^{206}Pb/^{204}Pb vs. CaO and b. ^{87}Sr/^{86}Sr vs. K$_2$O for OIB. HIMU (solid black circles) has the highest ^{206}Pb/^{204}Pb and CaO than all oceanic basalts (gray circles); it also has lower ^{87}Sr/^{86}Sr and K$_2$O than EMI and EMII basalts.

(Fig. 2a). The FOZO (or C) is argued to be a ubiquitous component in MORB and many OIB sources (e.g., Hanan and Graham, 1996). As discussed in detail below, FOZO is also proposed here to be the universal source of the basaltic foundation of ocean islands.

2.2. The new hypothesis

Marine carbonates, primarily CaCO$_3$, are ubiquitous in the ocean crust from Precambrian to present although their amount is highly variable, from being a minor component in calcareous sediments and altered MORB to being the major component in massive reefal limestone (e.g., Veizer and MacKenzie, 2003). Studies have shown that marine carbonates can be subducted deeper and transferred into the mantle wedge, at least, by downward moving fluids previously formed by carbonate dissolution at shallower depths (Frezzotti et al., 2011). Experimental results have also shown that variable amounts of carbonates embedded in pelites, basalts, peridotite, and carbonated serpentinites (ophiocarbonates) can survive the shallow level decarbonation process and partial melting in the upper mantle (Grassi and Schmidt, 2011; Kerric and Donelly, 1998; Yaxley et al., 1998). The survival of marine carbonates during subduction, perhaps in the form of dolomite and/or magnesite (MgCO$_3$), is especially higher along mature arc settings where old, cold oceanic crust is being subducted (Grassi and Schmidt, 2011). Evidence for some carbonates actually making it deep in the mantle is provided by the geochemistry of some diamonds and their melt plus solid inclusions. Some diamonds are clearly associated with oceanic metasedimentary rocks, contain isotopically heavy carbon that can be traced to crustal carbonate and, most importantly, contain actual carbonate (Brenker et al., 2007; Tappert et al., 2009; Walter et al., 2008). It has also been shown that some carbonatite xenoliths are derived from recycled marine carbonates (He et al., 2014).

The marine carbonate recycling hypothesis, henceforth called the new hypothesis, posits that some fragments of ancient limestone made it to the lower mantle and are now returning to the surface as a small degree partial melt component in OIB (Castillo, 2013a) and MORB (Castillo, 2013b). Most likely, with the addition of minor Fe, these transform into dolomite II and then dolomite III (the higher-pressure phases of CaCO$_3$) as these sink deeper into the mantle (Mao et al., 2011). Carbonated peridotite has a lower melting temperature than dry peridotite in the upper mantle (Dasgupta et al., 2013 and references therein) and carbonate-induced melting may occur in deeply subducted lithosphere at near-adiabatic temperatures in the Earth's transition zone and lower mantle (Rohrbach and Schmidt, 2011 and references therein). In other words, subduction of marine carbonates allows the generation of melts from carbonated silicate and/or carbonatite at various depths in the mantle. Some of the subducted marine carbonates return to the surface as carbonatite magma (e.g., in east Africa) through pooling of melts exsolved from carbonated peridotite (Dasgupta et al., 2006). Moreover, carbonate melt provides the metasomazing fluid and/or CO$_2$ flux in xenoliths in intraplate magmatism (e.g., Chauvel et al., 1997), in the lithospheric mantle source of alkaline OIB (e.g., Pilet et al., 2008), and at the onset of partial melting in the upper mantle (Dasgupta et al., 2013). The carbonated silicate or carbonatite melt is a small degree (a few %) partial melt and, thus, highly enriched in incompatible and volatile (e.g., CO$_2$, H$_2$O) elements derived from other recycled crust and surrounding mantle materials.

Marine carbonates are a more effective source of the distinct HIMU and FOZO compositions than altered MORB. If these are precipitated out of seawater in equilibrium, should have very high μ (>100,000) because U is abundant in seawater (>1 ppm) whereas Pb is low (0.003 ppb). Such a theoretical μ value, however, has never been measured in any CaCO$_3$ although modern marine carbonates indeed rarely contain Pb (and Th), but contain U (e.g., Edwards et al., 1987). Although U may not be abundant in Archaean seawater because of the reducing atmosphere during early Earth history, the few available Archaean carbonates from Zimbabwe do have high μ values (38–164) and correspondingly high ^{206}Pb/^{204}Pb ratios (30.17 to 104.37 — Collerson et al., 2002; Kamber et al., 2004). It is noteworthy, however, that these carbonates were most likely deposited in a restricted basin that may have compromised their U–Th–Pb and Rb–Sr isotope systematics and were also variably affected by alteration that tends to lower their μ and Pb isotopic values, similar to those of the country rocks. In any case, recycled marine carbonates or carbonatites had been proposed as the source of radiogenic Pb isotopic signatures of some OIB (e.g., Hoernle et al., 2002; Tatsumoto et al., 1984), but these have not been formally proposed as the systemic source of HIMU and particularly FOZO compositions. Equally significant, marine carbonates have one of the lowest Rb/Sr (0.005) among crustal rocks. Thus, marine carbonates have an inherent decoupling of U/Pb (+ U/Th) and Rb/Sr ratios. As detailed below, the new hypothesis also posits that K depletion (Fig. 3b) is part of the intrinsic properties of the proposed Archaean carbonate protolith for HIMU. In other words, subduction dehydration may affect CaCO$_3$ or carbonated rocks, but their intrinsic major and trace element composition mainly defines the source characteristics of HIMU and FOZO.

The broad, linear MORB-global OIB trend in the ^{206}Pb/^{204}Pb–^{207}Pb/^{204}Pb space has traditionally been given an age significance of about 2.0 Ga or younger (Faure, 1986), but others argue for an older age (e.g., Hanyu et al., 2011; Stracke et al., 2005). In the new hypothesis, linear trends of individual HIMU and FOZO basalt groups represent mixing mainly between the highly-radiogenic Pb in recycled marine carbonates and initial unradiogenic Pb isotopic compositions along the Earth's single-stage growth curve during or right after the formations of the carbonates. Basically these mixing trends are secondary stage isochrons, but only if the individual systems remained closed with respect to U and Pb (Faure, 1986). A simple illustration of this concept is shown by the steeper and, hence, older (3.2 Ga) ^{207}Pb/^{206}Pb linear trend of Mangaia (representing HIMU) basalts than the trend (0.7 Ga) of Canary (representing FOZO) basalts (Fig. 4a). The old age of the former is consistent with the proposed Archaean Pb model age for HIMU basalts by Nebel et al. (2013); see also, Hanyu et al. (2011). Moreover, the intersections of

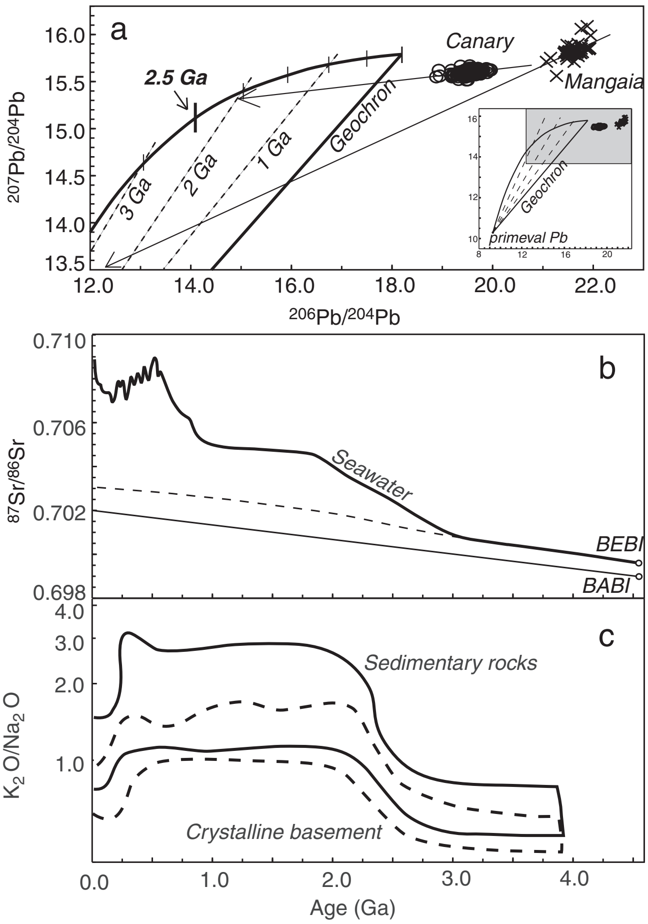

Fig. 4. a. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram illustrating one possible interpretation of the 'anomalous' Pb isotopic ratios of OIB from Mangaia and Canary islands. The intersections of the $^{207}Pb/^{206}Pb$ lines, fitted through the isotopic variations of these OIB, with the single-stage growth curve for the Earth with $^{238}U/^{204}Pb = 8.67$ (Galer and Goldstein, 1996) are the isotopic ratios of their respective sources before varying amounts of radiogenic Pb were added. The growth curve was derived from primeval $^{206}Pb/^{204}Pb = 9.3066$ and $^{207}Pb/^{204}Pb = 10.293$ ratios and 4.55 Ga age of the Earth. In each island group, the slope of $^{206}Pb/^{207}Pb$ line represents roughly the interval of time (Mangaia, about 3.2 Ga; Canary, about 0.7 Ga; Pb isotopic data are from the GEOROC database — http://georoc.mpch-mainz.gwdg.de/georoc/) that began with the formation of radiogenic Pb in its carbonate source, which had an 'inherently' very high μ, and terminated when such radiogenic Pb was mixed with the single-stage Pb ratio. Note the original very high μ was created by the subduction of ancient $CaCO_3$. b. Seawater $^{87}Sr/^{86}Sr$ deduced from marine $CaCO_3$ and c. K_2O/Na_2O of igneous and sedimentary rocks (Veizer and MacKenzie, 2003 and references therein) through time. BABI = basaltic achondrite best initial ratio; BEBI = bulk-Earth best initial.

the two linear trends with the single stage growth curve indicate an older (Archaean, ≥2.5 Ga) formation age of the source carbonate for HIMU than for the latter (post-Archaean, <2.5 Ga).

The Archaean primary age of HIMU is also consistent with the low $^{87}Sr/^{86}Sr$ ratio (≤0.702) of Archaean marine carbonates and increase of the radiogenic Sr component in carbonates since the Proterozoic (Fig. 4b). However, because the $^{87}Sr/^{86}Sr$ ratio of the bulk of FOZO is still quite low (≤0.704; Fig. 2a), the recycled carbonates in FOZO source should not be much younger than Proterozoic ($^{87}Sr/^{86}Sr \leq 0.705$; Fig. 4b) and most likely mix with a low $^{87}Sr/^{86}Sr$ component, such as recycled basaltic crust (e.g., Hanan and Graham, 1996) or pristine mantle (Collerson et al., 2010), but see more detailed discussions below. To a first order the proportion of Archaean limestone ($^{87}Sr/^{86}Sr = 0.702$; 500–1000 ppm Sr) needed to mix with the altered, underlying Archaean lithospheric mantle (e.g., $^{87}Sr/^{86}Sr = 0.7029$; 15 ppm Sr) to produce a HIMU mantle source ($^{87}Sr/^{86}Sr = 0.70285$) is rather small (0.021 or <5%). Significantly, the $^{87}Sr/^{86}Sr$ evolution of marine carbonates is mirrored by the K_2O/Na_2O secular compositional variations in the contemporaneous igneous and sedimentary rocks (Fig. 4c), consistent with the lower $^{87}Sr/^{86}Sr$ and K_2O of HIMU basalts compared to other OIB (Fig. 3b).

In summary, the opportune combination of age and composition data suggests that the distinct composition of classic HIMU is sourced from Archaean carbonates. Such an Archaean age is consistent with the presence of anomalous sulfur isotopic compositions indicating mass-independent fractionation (MIF) in olivine-hosted sulphides from Mangaia. Terrestrial MIF S isotope signatures were generated exclusively in the Archaean (Cabral et al., 2013). An Achaean age for FOZO is also evidently shown by recent Hf–Nd–Pb (Nebel et al., 2013) and Os (Day et al., 2014) isotopic data. In contrast, the less radiogenic Pb and more radiogenic Sr isotopic compositions of the more voluminous FOZO basalts are sourced from post-Archaean carbonates. The post-Archaean age of the FOZO isotopic signature is consistent with the suggestion that FOZO is simply a 'young HIMU' (Stracke et al., 2005; Thirlwall, 1997). Significantly, carbonatites derived from recycled post-Archaean marine carbonates occur in Canary and Cape Verde Islands (Hoernle et al., 2002). The new hypothesis is also highly consistent with the aforementioned lower SiO_2, but higher CaO/Al_2O_3, FeO^{total}, TiO_2, and especially CaO (Fig. 3a) contents of HIMU basalts compared to other OIB (Jackson and Dasgupta, 2008).

3. A conceptual model for the source of OIB

The unusually radiogenic Pb isotopic ratios of the bulk of oceanic lavas have created a major concern that has been termed the "Pb paradox" (Allegre, 1969; Allegre et al., 1988) or, simply, the HIMU effect (Stracke et al., 2005). The new hypothesis presented above posits that a small amount (a few %) of ancient marine carbonates is mainly responsible for the diagnostic $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ ratios and some of the distinctive chemical features (e.g., high CaO, low K_2O) of OIB with the most extreme (HIMU) and moderate HIMU effect (FOZO) in OIB (Castillo, 2013a). It may also be responsible for the HIMU effect or mildly radiogenic Pb isotopic signature of MORB (Castillo, 2013b). The latter is most likely accomplished through the upwelling of recycled marine carbonates from deep in the mantle, causing early and deep partial melting in the upper mantle (Dasgupta et al., 2013). The major question then is what is the bulk source material for OIB?

The following is a description of the full extension of the new (or marine carbonate recycling) hypothesis to explain the origin of the $^{208}Pb/^{204}Pb$, $^{143}Nd/^{144}Nd$, $^{177}Hf/^{176}Hf$, and $^{3}He/^{4}He$ characteristics of HIMU and FOZO. Basically, the extension is a conceptual model that claims the subducted oceanic lithospheric mantle (i.e., not the subducted oceanic crust) is the universal source of OIB whereas the post-Archaean upper mantle is the main source of modern MORB. Such a concept is constructed by putting together after some modifications established evolution models for the different isotope systems (Albarede, 2008; Class and Goldstein, 2005; Elliott et al., 1999; Jackson et al., 2008; Kerr et al., 1995; Niu and O'Hara, 2003; Salters and White, 1998) that are compatible with the predictions of the new hypothesis. Readers are referred to these publications for detailed descriptions of individual models. The detailed origin of the bulk major and trace element composition of OIB is beyond the scope of this study.

3.1. The bulk composition of OIB

All OIB and their differentiates originate from parental, primitive basaltic magmas and this requires a universal source that must be able to readily produce such primitive magmas. The new hypothesis adopts after some modifications the models of Kerr et al. (1995) and Niu and O'Hara (2003) claiming that the oceanic lithospheric mantle, the ubiquitous lower part of subducted slab, is the universal source of the basaltic foundation of ocean islands. End-member OIB types (EMI, EMII and HIMU) are simply from leftover crustal materials atop the lithospheric mantle after the slab has passed through the subduction process detailed below and shown in Fig. 5. The lithospheric mantle and overlying crust comprise the oceanic lithospheric plate or, simply, oceanic slab. Each end-member OIB type, particularly HIMU, cannot be produced by partial melting of a pure, crustal end-member source alone because such a source is generally incapable of producing primitive basaltic melt. Each end-member OIB type is also volumetrically small because the chances of preserving pure end-member sources, such as exclusively continental material for EMII or marine carbonates for HIMU, atop the oceanic lithosphere after the subduction process are rather small. In majority of cases, crustal materials and marine carbonates in particular are simultaneously present atop the lithospheric mantle such that their respective distinct characteristics counteract each other. That is, recycled crustal materials and lithospheric mantle mix and end up with an intermediate, mixed composition. Hence, OIB isotopic compositions converge to or are focused in a zone (Fig. 1). Notably, the oceanic crust subducted through time has been estimated to constitute about 5% of the mantle at present (Jackson and Dasgupta, 2008). The oceanic crust comprises only about 10% of the oceanic slab and, thus, there should be more than enough subducted lithospheric mantle to be the universal source of OIB.

Hart et al. (1992) described the universal source of OIB (or FOZO) as an actual parent or mantle reservoir that is never sampled in pure form. The new hypothesis claims that the oceanic lithospheric mantle is the main component of FOZO (the term is retained in the remainder of the discussion). It is always sampled, but is not an end-member source with distinct isotope characteristics (Figs. 1 and 5). That is, all OIB have a FOZO basaltic melt component. The afore discussed FOZO basalts with young HIMU Pb isotopic composition are the bulk of OIB that do not have extreme end-member compositions. Many authors disagree on the distinct isotopic composition of FOZO because its isotopic composition is evolving with time, as illustrated in Fig. 4b and c.

Fig. 5 illustrates the conceptual model. Similar to many proposed Earth evolution models, it assumes an initial BSE-like mantle and, then, an evolving depleted upper mantle starting at 2.5 Ga. FOZO (or the universal source of OIB) is the subducted oceanic lithospheric mantle overlain by "more enriched" basaltic crust and sediments. The topmost portion of lithospheric mantle is relatively depleted due to the extraction of the overlying basaltic crust, as evidenced in abyssal peridotites (Niu and O'Hara, 2003; Niu et al., 2002). Lots of seawater and sediments including marine carbonates are added to the oceanic slab as it transits to subduction zone. During subduction, the entire slab including the lithospheric mantle (e.g., Deschamps et al., 2013) dehydrates and this process takes away many incompatible trace elements such as large ion lithophile elements and Pb from the slab. The entire dehydrated package is termed "subduction component" (e.g., Tatsumi and Eggins, 1995). Whether some elements in the subduction component, particularly U, escape into the upper mantle (Elliott et al., 1999) and do not end up in arc crust, is permissible. Equally important, parts of the subducting crust may be removed tectonically by e.g., off-scrapping, accretion and/or underplating, and through partial melting. Finally, the slab undergoes transformation to eclogite and then to other higher-pressure and denser phase assemblages as it goes deep into the mantle, perhaps all the way to core-mantle boundary.

Such dehydration, variable removal of the enriched crust and metamorphic processes affect the overall composition of the subducted oceanic slab. First, these transform to generally anhydrous phases (e.g., garnet, pyroxene) almost all hydrous phases in the slab such as clay minerals in the crust and serpentines in the lithospheric mantle. Importantly, recent studies have considered that serpentinites are a significant, but often underestimated reservoir that provides geochemically enriched components to arc magmas (e.g., Deschamps et al., 2013). Thus, the production and eventual removal of subduction component from the oceanic slab through dehydration are a significant geochemical cleansing process that depletes the slab with many of its highly fluid- or even some melt-mobile, incompatible trace elements (Kessel et al., 2005). Second, the transformation is accomplished through a series of isochemical metamorphic reactions that reduce the number of unstable and metastable phases into a smaller number of stable metamorphic assemblages (e.g., Bebout, 2007; Vernon, 1975). These should occur in a 'closed' metamorphic environment that produces a dense and highly refractory slab that is generally shielded from partial melting, mixing and other mantle processes (e.g., Tolstikhin and Hofmann, 2005). These reactions also lock in the distinct composition of the lithosphere subducting at any given time and location, creating the compositional heterogeneity of OIB (Fig. 1). These reactions should also neutralize the strong subduction signature of the bulk of subducted lithosphere, by mixing the trace element content of the enriched crust with that of the underlying lithospheric mantle that has a depleted, magmatic signature (cf., Niu and O'Hara, 2003).

To briefly summarize, the geologic processes associated with oceanic slab subduction from surface to mantle including dehydration of subduction component, removal of the crust and metamorphism extract most of the geochemical enrichment in the subducting slab (cf., Porter and White, 2009). Combined with the extraction of basaltic melt from the uppermost lithospheric mantle, the subducted ultramafic

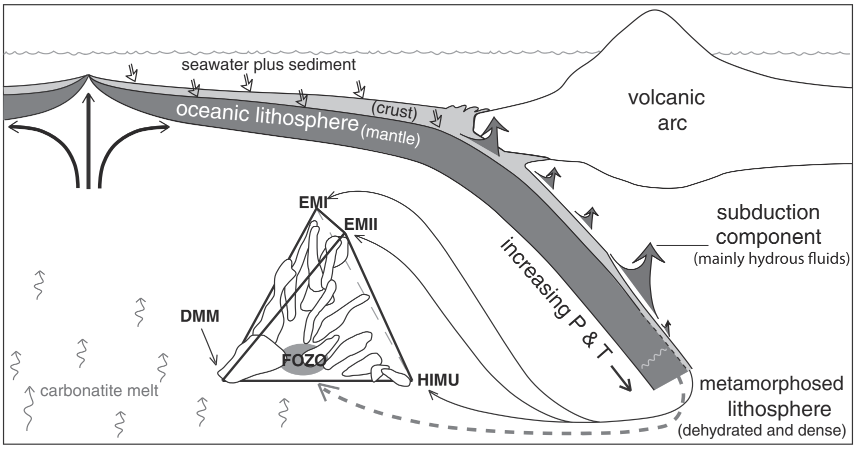

Fig. 5. Schematic diagram of a modified standard model for the origin of isotopically defined mantle components (Workman et al., 2004). The EMI, EMII and HIMU corners of the isotopic tetrahedron represent recycled crustal materials and these generally are mixing with FOZO, which represents the depleted, lithospheric mantle portion of the subducted slab. The DMM is the upper mantle that supplies melts to mid-ocean ridges. A small amount of carbonatite melt is coming from below. See text for more detailed discussions.

lithospheric mantle is generally depleted. The entire slab, however, is still capable of producing the compositional spectrum of primary OIB melts because of the variable amount and type of overlying crust that survive subduction. The effects of the removal of subduction component from the slab, including the retention of high-field strength elements (HFSE) such as Hf (discussed below) and depletion in Pb, are preserved although, in general, most of the strong subduction effects should have been neutralized (cf., Niu and O'Hara, 2003). Thus, the full extension of the marine carbonate recycling hypothesis envisions the subducting oceanic slab as a metamorphic environment with an open-system, hydrated and relatively enriched protolith that ends up as a closed-system, dehydrated and generally depleted metamorphosed slab (Bebout, 2007).

3.2. The ^{208}Pb/^{204}Pb ratios of HIMU and FOZO and the 'kappa conundrum'

As mentioned earlier, the HIMU ^{208}Pb/^{204}Pb–^{206}Pb/^{204}Pb linear array (Fig. 2b) suggests a Th/U ratio (more properly, ^{232}Th/^{238}U or κ value) lower than that defined by the MORB isotopic array. The latter is remarkably homogeneous ($\kappa = 3.8$; κ values are from Elliott et al., 1999) and lower than BSE ($\kappa = 4.0$), but higher than what is actually measured from MORB samples that, by inference, represents DMM ($\kappa = 2.5$). Such differences in κ values among DMM, MORB array and BSE are the second paradox caused by the highly radiogenic Pb isotope ratios of the bulk of oceanic lavas and has been termed the "kappa conundrum" by Elliott et al. (1999; see also, Zartman and Richardson, 2005). As a possible solution, Elliott et al. proposed a model that requires a κ value for the mantle that was roughly constant during early Earth history, but steadily decreases from the Proterozoic to present. They claimed that this is due to the preferential, post-Archaean U recycling (PURE), relative to Th, back into the upper mantle. This occurred due to the marked increase in atmospheric oxygen fugacity at 2.2 Ga, causing high aqueous mobility of U in the oxidizing environment at the Earth's surface.

In the new hypothesis, HIMU has high U/Pb because of its high U content and, thus, its Th/U or κ value is low, less than that of the MORB isotopic array (3.8). Thus, the high U content of recycled carbonates can offer simultaneous reasonable solutions to both the high U/Pb (first Pb paradox; Fig. 4a) and low Th/U (second Pb paradox or kappa conundrum; Fig. 6a) observed in HIMU as well as the overall κ values of oceanic lavas (discussed below). Notably, such a claim is hard to justify by the current model for the source of HIMU end-member that claims that the high U/Pb ratio comes from the loss of Pb, not an increase in U. In the new hypothesis, the κ value of FOZO is variable, ranging from HIMU-like to BSE-like, because variable amounts of the ubiquitous post-Archaean marine carbonates atop the subducted slab are mixing with other crustal materials with variable ages and Th/U ratios. For example, OIB with strong EMI and EMII affinities have lower ^{206}Pb/^{204}Pb but at the same time higher ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb for given ^{206}Pb/^{204}Pb ratios than HIMU (e.g., Hofmann, 2003; White, 2010). This is because their enriched crustal sources have high Th/U ratios that tend to neutralize the low Th/U of marine carbonates. Finally, the measured κ value from the MORB ^{208}Pb/^{204}Pb–^{206}Pb/^{204}Pb linear array, in turn, results from a mixture of recycled U (from post-Archaean carbonates) and DMM, as also called for by the PURE model.

However, there are a couple of major disagreements between the new hypothesis and PURE model. They strongly disagree on the origin of the uranogenic Pb isotopic signature of oceanic lavas as the PURE model posits that such a HIMU effect is mainly coming from recycled MORB (Elliott et al., 1999). The other discrepancy pertains to the key requirement of the PURE model that a single change in the κ value of the upper mantle occurred at 2.2 Ga, whence oxidized U started to be preferentially recycled back into the 'open-system' upper mantle at subduction zone. On the other hand, the new hypothesis maintains that the major turning point in the history of the sources of oceanic lavas is at 2.5 Ga (Figs. 4a, b, c and 6a). This is most likely the time when the initial κ value of the upper mantle started to decrease (e.g., Zartman and Richardson, 2005). Although the return of U to the upper mantle beneath subduction zone is permissible in the new hypothesis, it prefers that additional recycled U and its radiogenic Pb daughter return to the upper mantle from the deeper mantle, producing the HIMU effect in modern MORB (Castillo, 2013b), at <600 Ma during or right after the Proterozoic–Phanerozoic boundary (see additional arguments by Galer and O'Nions, 1985). This occurs because of the influx from the deep mantle of carbonatitic melt (Dasgupta et al., 2013) that is enriched in e.g., U and radiogenic Pb. The main reason for such a Phanerozoic return of additional recycled U in the upper mantle is that U decays to radiogenic Pb. Consequently, if U has been returning back in the upper mantle since 2.2 Ga (Elliott et al., 1999), then some modern MORB should have highly radiogenic Pb isotopes, close to those of HIMU. However, the ^{206}Pb/^{204}Pb of the bulk of modern MORB is <19.8 (Hanan and Graham, 1996).

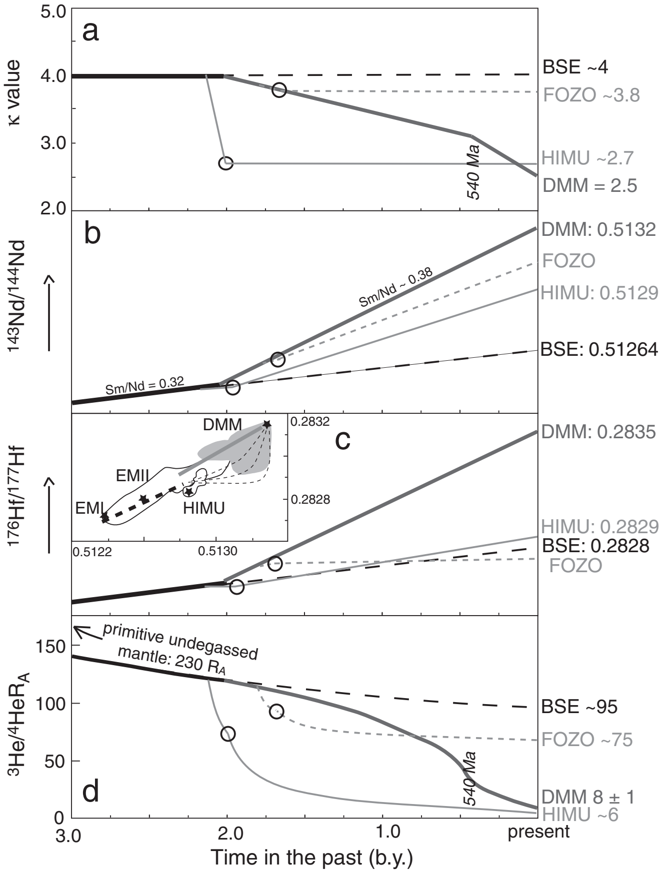

Fig. 6. Schematic evolution diagrams for the different chemical/isotopic systems discussed in the text. a) Modified post-Archean uranium recycling (PURE) model (Elliott et al., 1999). HIMU κ value was calculated using a 0.7128 slope of the Mangaia ^{208}Pb/^{204}Pb–^{206}Pb/^{204}Pb array and 3.2 Ga ^{207}Pb/^{206}Pb isochron age (from Fig. 4). b) Idealized ^{143}Nd/^{144}Nd evolution; not to scale to emphasize the modern separations among DMM, FOZO, HIMU, and BSE. c) Idealized ^{176}Hf/^{177}Hf evolution; also not to scale to emphasize the modern separations among DMM, FOZO, HIMU, and BSE. The global correlation between ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf is summarized in the inset figure. White field represents OIB whereas gray field represents MORB. d) Modified ^{3}He/^{4}He evolution model of Class and Goldstein (2005). In all diagrams, circles in HIMU and FOZO lines represent time of subduction. See text for more detailed discussions.

Fig. 6a illustrates the general concept of producing the range of κ values of modern oceanic lavas using the modified PURE model of Elliott et al. (1999). The early mantle has a BSE-like, constant κ value of 4.0 until the end of Archaean (Zartman and Richardson, 2005). This is the source of subducted Archaean oceanic lithospheric mantle. In the case of HIMU the lithosphere is topped by a small amount (a few %) of Archaean marine carbonates with high U content — producing

OIB with a low κ value (2.7 calculated for Mangaia). As in many standard Earth models, the post-Archaean upper mantle starts to become more depleted producing e.g., lower Rb/Sr, Nd/Sm, Hf/Lu, and Th/U ratios than BSE. The actual κ value of the post-Archaean upper mantle is unknown, but it is the main source of the Pb isotopic composition of the bulk of FOZO. Oceanic lithosphere derived from it also contains marine carbonates (with high U/Pb), but the resultant κ values in OIB range from HIMU-like to BSE-like, depending upon the amount of enriched material that contains higher Th/U than marine carbonates. Finally, the upper mantle reaches the current κ value of 2.5 fairly recently because of the migration of small degree carbonatite partial melt in the upper mantle (Dasgupta et al., 2013). The new hypothesis posits that such an event occurs in the Phanerozoic, and this is represented by a 'kink' in the post-Archaean Th/U evolution line of the upper mantle.

3.3. The ^{143}Nd/^{144}Nd ratios of HIMU and FOZO and the 'Hf paradox'

The ^{143}Nd/^{144}Nd ratio of HIMU (0.51285) is higher than BSE (typically 0.51264 — cf., Caro and Bourdon, 2010). That of FOZO is also higher than BSE, but there are differences in opinion on its true composition (e.g., Hanan and Graham, 1996; Hart et al., 1992; Hauri et al., 1994; Stracke et al., 2005). These ^{143}Nd/^{144}Nd ratios indicate that both HIMU and FOZO sources are not primordial and they record ancient geochemical depletion (e.g., producing higher Sm/Nd ratio than BSE). A valid explanation for such Nd isotopic signatures (and also of Hf isotopes, which behave similarly as Nd isotopes) is that HIMU and FOZO are ancient depleted mantle-derived melts (Salters and White, 1998). This notion was rejected because peridotite melting cannot at the same time explain the Rb–Sr and U–Th–Pb isotope systematics of HIMU and FOZO (Stracke et al., 2005). Such a counter-argument, however, becomes irrelevant if recycled marine carbonates indeed effectively control the ^{87}Sr/^{86}Sr, ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb signatures of HIMU and FOZO (Fig. 4) whereas the temporal evolution of the κ value controls their ^{208}Pb/^{204}Pb signature (Fig. 6a). Thus, the new hypothesis concurs that the source of the ^{143}Nd/^{144}Nd signature of HIMU and FOZO is an ancient depleted source (Salters and White, 1998). Such a source, however, is the subducted depleted lithospheric mantle (Fig. 5) instead of either an isolated, significant amount of ancient (b.y.) MORB or fractionated and isolated small amounts (<1%) of perovskite during the early history of the Earth (Salters and White, 1998).

Fig. 6b illustrates the general concept of producing the high ^{143}Nd/^{144}Nd signature of HIMU and one of the many possible paths of FOZO. The Sm/Nd ratio of Archaean oceanic lithosphere produced from partial melting of the BSE mantle (Sm/Nd = 0.32) is low (<0.32), but the overall geochemical depletion effect of the subduction process variably, but generally increases it slightly (≥0.32). The lithosphere becomes a closed system during and/or right after subduction and remains closed as it travels into the deep mantle. The decay of ^{147}Sm to ^{143}Nd inside the subducting lithosphere during the isolation period produces the present ^{143}Nd/^{144}Nd of HIMU. The production of the ^{143}Nd/^{144}Nd ratio of the bulk of FOZO is quite similar to the above scenario except that the upwelling mantle after the Archaean continuously becomes depleted (time-integrated Sm/Nd of 0.38; see also Figs. 4b, c and 6a). Consequently, the resultant depleted lithospheric mantle (Sm/Nd ≤ 0.38) produces a range of ^{143}Nd/^{144}Nd compositions that can be as low as BSE to almost as high as MORB. The general exception to this rule is subducted slab that still contains too much enriched crustal materials even after the subduction process. The latter ends up producing OIB with lower ^{143}Nd/^{144}Nd than BSE, or with extreme EMI or EMII flavors.

A similar scenario is proposed for the evolution of ^{176}Hf/^{177}Hf in HIMU and FOZO (Fig. 6c). The subduction process also decreases the Hf and other HFSE contents of the subducted slab although to a much lesser extent than LILE. This is clearly evident in subduction zone magmas, which have hallmark depletions in HFSE relative to LILE (e.g., Tatsumi and Eggins, 1995). However, the residual relative HFSE enrichment is countered by the transformation of the subducting slab into eclogite (omphacite–garnet metamorphic assemblage), which has a strong affinity for heavy REE, including Lu (e.g., Green et al., 2000). Thus, although the Lu/Hf ratio of the slab is high, it is relatively lower compared to the Sm/Nd ratio. This is clearly evident in the anomalously low ^{176}Hf/^{177}Hf for a given ^{143}Nd/^{144}Nd ratio of HIMU relative to other oceanic lavas (Salters and White, 1998; see also, inset in Fig. 6c) because its source is mainly subducted lithospheric mantle topped by a small amount (a few %) of Archaean marine carbonates. On the other hand, the bulk of subducted slab contains other residual enriched crustal materials as well and, thus, the HFSE-enriched, subduction signature of the slab is variably reduced, producing the bulk of OIB (or FOZO) with extremely well correlated ^{176}Hf/^{177}Hf–^{143}Nd/^{144}Nd isotopic signatures (Salters and White, 1998). In contrast, the Lu/Hf ratio of MORB evolves separately, and reflects the time-integrated depletion of the upper mantle mainly through partial melting (i.e., purely magmatic process) such that the Lu/Hf (and Sm/Nd) fractionation depends only on the relative incompatibilities of Lu and Hf (plus Sm and Nd) with respect to the mantle (e.g., Shaw, 1970).

Significantly, the above mechanism for the evolution of ^{176}Hf/^{177}Hf in HIMU and FOZO offers an alternative explanation for the origin of the so-called Hf paradox (Patchett and Tasumoto, 1980; Salters and Hart, 1989). The paradox pertains to the observation that although ^{176}Hf/^{177}Hf and ^{143}Nd/^{144}Nd correlate, the slope of MORB array is steeper, covering about 60% of the ^{176}Hf/^{177}Hf range but only 30% of the ^{143}Nd/^{144}Nd of oceanic lavas, compared to that of OIB (Dickin, 1997; Salters and Hart, 1989). Moreover, the correlation is more coherent in OIB than in MORB. As before, the new hypothesis posits that the universal source of OIB is the subducted oceanic lithosphere mantle, which generally has high ratios of Sm/Nd, Sr/Rb and, to a certain extent, Lu/Hf. In the new hypothesis, the ^{176}Hf/^{177}Hf variations of oceanic lavas are not a garnet signature in the source of MORB (Salters and Hart, 1989), but instead a counter-intuitive consequence of garnet stability plus Hf enrichment in the subducted slab (Fig. 5). That is, the increase in the ^{176}Hf/^{177}Hf ratio of OIB sources, particularly that of HIMU, is slower than that of the more homogeneous DMM source of MORB because of their slightly lower Lu/Hf ratios. Thus, HIMU and the bulk of FOZO are near DMM in terms of ^{143}Nd/^{144}Nd but closer to BSE in terms of ^{176}Hf/^{177}Hf ratio. The retarded ^{176}Hf/^{177}Hf evolutionary trend of the bulk of OIB is qualitatively shown by the dash thick line whereas the normal ^{176}Hf/^{177}Hf evolutionary trend of DMM plus OIB with least HIMU effect by the solid gray line in the inset in Fig. 6c. The steep or sub-vertical array of some modern MORB is due to mixing between DMM and small degree carbonatite partial melts in the deep upper mantle (Fig. 5). Such mixing is again the HIMU effect in MORB (Castillo, 2013b) and represented by the dash curved lines between DMM and young HIMU in the inset in Fig. 6c.

3.4. The high ^{3}He/^{4}He ratio of some FOZO basalts

As also noted earlier, OIB with the highest ^{3}He/^{4}He ratio (up to 50 R_A, where R_A = sample ^{3}He/^{4}He relative to air ratio) are within the FOZO region (Fig. 1). MORB has the canonical value of the upper mantle, which is 8 ± 1 R_A (Graham, 2002). Jackson et al. (2007) have shown that EMII, mainly derived from recycled continental material, has ^{3}He/^{4}He ratio less than that of MORB. The ^{3}He/^{4}He of HIMU is also less than that of MORB because it is old and contains too much U that decays to radiogenic ^{4}He (^{4}He*). As of yet, there is no consensus on the source of the end-member EMI (Fig. 1), but available data for fresh volcanic glasses from Pitcairn Seamounts, its best representatives, show ^{3}He/^{4}He similar to that of MORB (Honda and Woodhead, 2005). These observations pose big geodynamic problems —what is the origin of the high ^{3}He/^{4}He signature and why does FOZO have some of the highest ^{3}He/^{4}He ratios (e.g., Albarede, 2008; Anderson, 1997; Class and Goldstein, 2005; Jackson et al., 2008; Porcelli and Elliott, 2008; Tolstikhin and Hofmann, 2005)?

The new hypothesis adopts a model modified from those of Class and Goldstein (2005), Albarede (2008) and Jackson et al. (2008) to explain the occurrence of OIB with high $^3He/^4He$ in FOZO (Fig. 6d). Class and Goldstein (2005) showed that MORB and OIB have striking chemical and isotopic similarities. As presented above, this is due to the notion that the lithospheric mantle source of OIB and upper mantle source of MORB share a common history of geochemical depletion through extraction of enriched components. However, they experienced different depletion processes and the effects are clearly reflected in their isotopic signatures (Figs. 4 and 6a to c). Another difference is although Class and Goldstein's model ends with a search for a mechanism to isolate plume sources of OIB, it also implies that the OIB source represents a portion of the mantle that was subjected to geochemical depletion due to the formation of continents and ocean crust throughout Earth history. In contrast, the new hypothesis posits that the high-pressure phase transformation of the oceanic slab during subduction isolates the depleted oceanic lithosphere (Fig. 5). This transformation keeps the slab a closed metamorphic system for a long while (1–3 b.y.) deep in the mantle.

Fig. 6d illustrates the general concept of producing the low $^3He/^4He$ signature of HIMU (solid thin line) and the high $^3He/^4He$ signature of some FOZO basalts (dash line). The latter is very similar to the model for the origin of high $^3He/^4He$ OIB proposed by Jackson et al. (2008). As Class and Goldstein (2005) proposed, the mantle $^3He/^4He$ decreases continuously with time from a primitive, undegassed value of 230 R_A due to a combination of irreversible loss of He to space by outgassing through magmatism and by *in situ* production of $^4He^*$ from the decay of U and Th. In the new hypothesis, He is assumed to be similar to other incompatible trace elements in that during partial melting of the peridotite mantle to create the oceanic crust, most of the He partitions into the basaltic melt (and eventually ends up in outer space), but some of it remains in the mantle residue that forms the lithospheric mantle beneath the basaltic crust. Significantly, He could potentially survive the subduction process because it can be trapped within defects in the mineral grains even in highly deformed peridotites (Kurz et al., 2009). Albarede (2008) has proposed a similar, though more quantitative model of trapping ancient He with high $^3He/^4He$ ratios in refractory rocks such as dunites in residual, old fragments of oceanic lithosphere and cumulates from the magma ocean. However, Albarede's proposals to preserve these refractory reservoirs, as stretched layers of variable thicknesses in the mantle, and to sample their trapped He later, through smaller degrees of partial melting, are very different from the ones envisioned by the new hypothesis. Interestingly, the highest $^3He/^4He$ ratios measured thus far (up to 75 R_A) are from picritic rocks (Stuart et al., 2003). Although these clearly suggest an ultramafic source, they were produced by relatively high degree of partial melting (cf., Albarede, 2008). The new hypothesis additionally assumes that the inventory of He in early Earth was higher than today such that the volume of trapped He in ancient lithosphere is still high relative to the present inventory. However, if hydration of the lithosphere is indeed significant (e.g., Deschamps et al., 2013), then only a small percentage of OIB would possess extremely high ($\gg 8\ R_A$) $^3He/^4He$ ratios (cf., Jackson et al., 2008). This notion is consistent with the scarcity of such OIB with extreme $^3He/^4He$ ratios as well as coexistence of high- and low-$^3He/^4He$ basalts in high $^3He/^4He$ ocean islands.

As before, the ancient lithospheric mantle containing He with high $^3He/^4He$ ratio is a closed metamorphic environment. The trapped $^3He/^4He$ decreases with time because of *in situ* production of $^4He^*$, but unlike the upper mantle, the isolated lithospheric mantle does not additionally suffer continuous outgassing or volcanism (see also, Jackson et al., 2008). Thus, the new hypothesis posits that the overriding factor dictating the rate of $^3He/^4He$ decrease in the subducting lithosphere is the amount of trapped Th and U; the latter is mainly dependent upon the amount of trapped marine carbonates. Such a key argument is indeed observed although with a lot of exceptions. OIB with the highest $^3He/^4He$ have lowest $^{206}Pb/^{204}Pb$ (proxy for U content) and $^{208}Pb/^{204}Pb$ ratios as well as Th content, such as those from Hawaii and Iceland, than OIB with lowest $^3He/^4He$, such as those from Mangaia, Tubuai and St. Helena (Class and Goldstein, 2005). In other words, all OIB sources experience the HIMU effect, making the $^3He/^4He$ ratios of OIB variable and irrespective of age (cf., Class and Goldstein, 2005). Notably, the high U content of OIB sources is consistent with the general similarity of the κ (Fig. 6a) and $^3He/^4He$ (Fig. 6d) evolution curves of HIMU and FOZO. The former has the lowest modern κ and $^3He/^4He$ values among OIB whereas the latter can have the highest. In contrast, MORB has a uniform and low $^3He/^4He$ (κ and Pb isotopic) values because DMM is an 'open' system suffering from continuous and constant production of $^4He^*$ and continuous extraction of partial melt through magmatism. Moreover, the upper mantle experiences later addition of carbonatitic melt containing U. Thus, the $^3He/^4He$ curve, similar to the κ curve, has a kink during the Phanerozoic (Fig. 6a and d). Finally, FOZO is not an end-member source and, thus, high $^3He/^4He$ OIB do not have a unique or distinct composition, as is indeed clearly shown by the variable compositions of high $^3He/^4He$ OIB from e.g., Hawaii, Iceland and Galapagos.

It is important to note, however, that the new hypothesis is clearly incorrect if the Class and Goldstein's model for the evolution of $^3He/^4He$ ratios does not reflect the best behavior of He in the mantle. Instead, it is possible that $^3He/^4He$ ratios decreased more rapidly early in Earth history such that any high $^3He/^4He$ ratios observed in OIB today could have only be preserved from a mantle isolated for, at least, 3 b.y. (Porcelli and Elliott, 2008). Thus, alternative models that store such high $^3He/^4He$ signatures in the core or in a deep layer in the mantle become more relevant. It is also noteworthy, however, that available analyses thus far show the ratio of the two primordial ^3He and ^{38}Ar isotopes appears to be constant (e.g., Graham, 2002). This relationship provides additional constraints on He evolution in the mantle as it indicates that the observed systematic variations of $^3He/^4He$ with $^{206}Pb/^{204}Pb$ and Th values, which are hypothesized here to be dependent upon the content of recycled marine carbonates within individual mantle source reservoirs, may indeed be primarily due to long-term production of $^4He^*$ within individual reservoirs. Significantly, the proposed model for a more rapid decrease of $^3He/^4He$ in the mantle is based simply on back-extrapolation from the current upper mantle $^3He/^4He$ ratio of $8 \pm 1\ R_A$ (Porcelli and Elliott, 2008). This model, however, does not take into account the decrease of κ value initially at 2.5 Ga and, then, at 540 Ma (Fig. 6a) most likely due to recycling of U. This, in turn, may have decreased $^3He/^4He$ in the Proterozoic and, then, Phanerozoic (Fig. 6d) in the upper mantle.

4. Geodynamic implications and concluding remarks

The presence of dense and cold recycled oceanic slabs in the lower mantle containing a few % marine carbonates or carbonatites plus their melts should make such slabs physically or thermally and compositionally distinct compared to the high-pressure phases and/or phase assemblages in the lower mantle. Consequently, they could possess an anomalous seismic velocity and may provide explanation for some of the observed lateral variations of seismic velocity in the lowermost mantle (e.g., Garnero, 2000). Moreover, partial melt from the carbonates/carbonatites could act as messenger as well as lubricant, if not propellant, of subducted slab materials from the lower mantle (e.g., Castillo, 1988) and, thus, recycling of carbonates plays a significant role in the convection process. This is evidently shown by e.g., the trace amount of recycled carbonate in the source of Hawaiian lavas (e.g., Hofmann et al., 2011; Huang et al., 2009) despite having the least HIMU effect among OIB. Moreover, marine carbonate recycling is consistent with the presence of carbonatite (and/or its melt) in the large, low-seismic velocity region in the lower mantle beneath Africa (i.e., African Superplume; Hansen et al., 2012) that, in turn, can explain the carbonatite-related magmatism along the East African Rift System (Castillo et al., 2012, 2014) and the connection between continental and oceanic carbonatites (e.g., Hoernle et al., 2002). The long-term interaction of marine carbonate-bearing mantle plume(s) with the Gondwana lithosphere may also shed some light on the continental lithospheric signature in south Atlantic mantle plumes (e.g., Hawkesworth et al., 1990). Finally, the marine carbonate recycling hypothesis also posits that many of the upwelling mantle plumes need not necessarily be 'hotter' than the ambient mantle because they contain variable amounts of recycled carbonates, meaning these plumes should be more volatile-rich (e.g., CO_2- and H_2O-rich) than the surrounding mantle.

The ideas presented in this paper are largely qualitative and the aforementioned few available data for Archaean carbonates from Zimbabwe do not necessarily preserve their true U/Pb and Pb isotopic ratios (e.g., Kamber et al., 2004). Thus, the marine carbonate recycling hypothesis and its full extension will be viewed with a lot of skepticisms. Given their large potentials to unlock the history and evolution of the Earth's mantle, however, future quantitative testing of the hypothesis should be done using available and new OIB data and when the amount and unmodified composition of Precambrian carbonates become better constrained.

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