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A proposed new approach and unified solution to old Pb paradoxes

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ABSTRACT

One of the most remarkable features of many and, perhaps, all oceanic basalts is that their Pb isotopic ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) are too radiogenic to be coming from the undifferentiated mantle or bulk silicate Earth. This has created three major concerns in the behavior of U, Th and Pb in the Earth's mantle that have been termed the Pb paradoxes. These are the unexpectedly long time-integrated high U/Pb (1st paradox), long time-integrated low Th/U (2nd paradox) and constant Ce/Pb and Nb/U (3rd paradox) in the mantle sources of oceanic basalts. The origins of such unexpected ratios have been the object of intense studies that produced several highly significant, but generally individualized results during the last four decades. Detailed analysis of available data shows that the paradoxes are closely interrelated as they all pertain to the mantle and have many common characteristic features. Thus, the Pb paradoxes constitute a system of equations that must be solved all together as each solution must satisfy every equation in the system. For example, compositional data for the voluminous mid-ocean ridge basalts (MORB) show that the 1st and 2nd paradoxes exhibit a long time-integrated enrichment of U and the Th/U and Nb/Th ratios are also constant. A single solution to simultaneously explain the paradoxes in MORB is possible if recycled materials with variable enrichments in incompatible trace elements, particularly U and its daughter Pb* plus Nb, Ce, and Th are added to or mixed with the depleted upper mantle. Significantly, a similar binary mixing solution has been proposed for the Pb paradoxes in ocean island basalts.

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1. Introduction

The discovery of the highly radiogenic Pb (Fig. 1) and variable Sr isotopic ratios of young oceanic basalts indicates that the mantle has been compositionally heterogeneous for a long (b.y.) time (Gast et al., 1964). Continuing Sr–Nd–Pb isotopic studies show that to a first order, the heterogeneous mantle can be described in terms of four distinct end-member sources and that the compositional spectrum of oceanic basalts results mainly from variable degrees of partial melting and mixing of these end-members (Hart et al., 1992; Hofmann, 2003). The increase in $^{206}Pb/^{204}Pb$ is due to the decay of radioactive isotope ^{238}U over time and, thus, the highly radiogenic Pb isotopes of oceanic basalts, consisting of mid-ocean ridge basalts (MORB) and ocean island basalts (OIB), imply that one of the end-members has a long time-integrated U/Pb (more properly, high $^{238}U/^{204}Pb$ or high μ–HIMU) ratio that is much higher than the bulk silicate Earth (BSE) (Allegre, 1969; Allegre et al., 1986). Specifically, OIB with extremely radiogenic Pb isotopes from St. Helena, Mangaia and Tubuai islands are purportedly derived from a HIMU end-member source. The other proposed mantle end-member sources for OIB are the geochemically enriched mantle 1 (EM1) and enriched mantle 2 (EM2) whereas the geochemically depleted mantle is the proposed end-member source for MORB (DMM). As

the bulk of oceanic basalts possess highly radiogenic Pb isotopic ratios that plot to the right of the geochron (Fig. 1), the proposed EM1, EM2 and DMM end-members also have the so-called HIMU effect (Vidal, 1992; Stracke et al., 2005; Castillo, 2015).

The high U/Pb ratio of the mantle sources of oceanic basalts is unexpected given that U is more incompatible than Pb and it is already enriched in the mantle-derived continental crust. This has given rise to a major concern regarding the concentration and behavior of U and Pb in the mantle that has been termed the main or 1st Pb paradox. Moreover, the decay of radioactive ^{232}Th increases $^{208}Pb/^{204}Pb$, which when plotted against $^{206}Pb/^{204}Pb$ ratios gives Th/U (or more properly $^{232}Th/^{238}U$ or κ) ratios for all oceanic basalts that are lower than the BSE κ value of ca. 4 (Tatsumoto, 1978; Galer and O'Nions, 1985; Elliott et al., 1999; Turcotte et al., 2001). Such low κ characteristics of oceanic basalts comprise the 2nd Pb paradox, which has also been termed 'kappa conundrum' (Elliott et al., 1999). Finally, Ce/Pb and Nb/U ratios have been observed to be constant (Hofmann et al., 1986). The constancy of the ratios is also unexpected given the known geochemical behaviors of Ce relative to Pb and Nb relative to U and, since both U and Pb are involved, has been termed the 3rd Pb paradox (Hofmann et al., 1986; Hofmann, 2003; Sims and DePaolo, 1997; Hart and Gaetani, 2006).

Significant efforts have been made to understand and solve the Pb paradoxes in the past three to four decades. However, the paradoxes were generally approached separately, resulting into a number of highly satisfactory and, thus, generally accepted albeit independent

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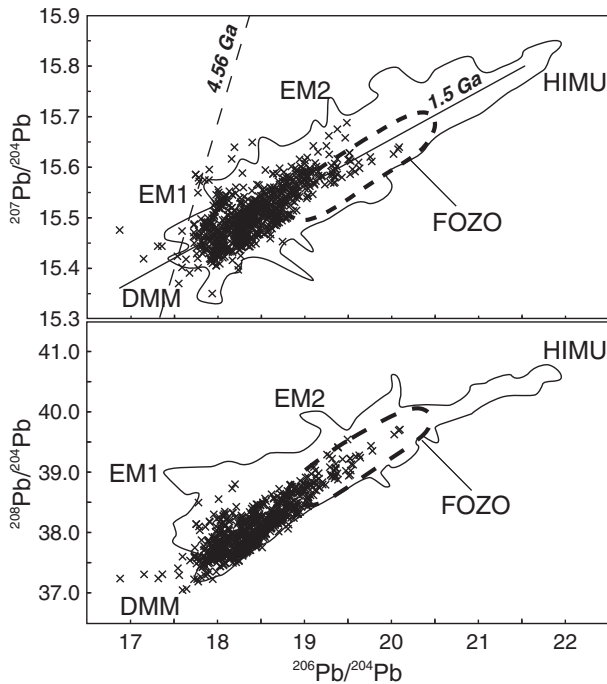
Fig. 1. (a) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ and (b) $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ for oceanic basalts. Field for OIB is from Stracke (2012) and data for ALL MORB are from Gale et al. (2013). Also shown are 4.56 Ga geochron (White, 2010) and proposed DMM, EM1, EM2, HIMU, and FOZO mantle components (Hart et al., 1992). The ALL MORB $^{207}Pb/^{206}Pb$ array in (a) has a slope of 0.9146 and this gives an apparent age of 1.5 Ga.

explanations. Proposed solutions to the 1st paradox include the transfer of Pb into the core (Oversby and Ringwood, 1971; Vollmer, 1977; Vidal and Dosso, 1978; Allegre et al., 1986), preferential retention of Pb relative to U in the lower continental crust or subcontinental lithosphere (e.g., Doe and Zartman, 1979; Kramers and Tolstikhin, 1997) or in residual mantle sulfide (Hofmann, 2003; Hart and Gaetani, 2006), hydrothermal transfer of Pb from mantle to continental crust (Peucker-Ehrenbrink et al., 1994; Chauvel et al., 1995; Hofmann, 2003), preferential recycling of U into the mantle since Early Proterozoic (e.g., Staudigel et al., 1995; Hofmann, 2003), and crustal contamination of an early-formed (roughly 4.55–4.45 Ga) terrestrial mantle reservoir (Jackson et al., 2010). By and large, majority of the proposed solutions center on the decrease in Pb, not on the increase in U, in generating the 1st Pb paradox (Hofmann, 2003). Consequently, a number of later efforts to solve the 1st paradox have shifted focus to the search of the 'low µ' reservoir that complements the HIMU source (Murphy et al., 2003; Hofmann, 2003; Burton et al., 2012).

Proposed solutions for the 2nd paradox, on the other hand, center on the relative behavior of U to Th. These include a simple two-stage Th/U depletion model of the upper mantle (Galer and O'Nions, 1985) with a primitive, first stage κ value of BSE of ca. 4 changing abruptly to a second stage value of DMM at ca. 2.5, a continuous evolution model in which κ started from a reasonable BSE composition but decreased with time due to continental extraction (Tatsumoto, 1978; Allegre et al., 1986), and the aforementioned preferential recycling of U into the mantle due to oxidizing conditions at the Earth's surface since Early Proterozoic (Elliott et al., 1999; Andersen et al., 2015).

Finally, the constancy of Ce/Pb and Nb/U ratios or 3rd Pb paradox has been proposed as due to homogenization of the mantle through convective stirring later in Earth's history (Hofmann et al., 1986; Hofmann, 2003). Alternatively, it is due to similar silicate mantle-melt partition coefficient values (K_d) for Ce and Pb as well as for Nb and U during magmatic processes although most experimental studies show that Pb and U are more incompatible than Ce and Nb, respectively, in silicates (Sims and DePaolo, 1997), or for Ce/Pb (or Nd/Pb), retention of Pb in

residual mantle sulfide during melting such that the bulk partitioning of Pb becomes equal to that of Ce (or Nd—Hart and Gaetani, 2006).

The main objective of this manuscript is to propose a new approach and a unified solution to the Pb paradoxes in oceanic basalts. This manuscript differs from the numerous significant solutions that have been published in three major ways. First, in contrast to the majority of prior studies, it introduces as well as emphasizes that the paradoxes are intricately connected to each other and to the radiogenic Pb isotopic composition of oceanic basalts. This simultaneous approach, in turn, necessitates related solutions. Second, focusing on the upper mantle, the approach shows that a unified solution to the Pb paradoxes in MORB is possible through binary mixing between small amounts of carbonatitic silicate melts (or their metasomatically-generated mantle phases) variably enriched in components derived mainly from the subducted crust through very low degree partial melting of the subducted oceanic lithosphere or slab and DMM (or its melt). Finally, a similar solution to the Pb paradoxes in OIB has already been proposed by the marine carbonate recycling hypothesis (Castillo, 2015). Thus, binary mixing between depleted and enriched mantle components presents a unified solution to the Pb paradoxes in both MORB and OIB.

In summary, the manuscript presents simple ideas and does not contain quantitative modeling of the paradoxes. The proposed solution is also not new as binary mixing of mantle sources in one form or another to explain the heterogeneity of oceanic lavas has long been proposed. For example, an early model to explain the wide spectrum of OIB compositions argued for binary mixing between the primitive or enriched lower mantle and depleted upper mantle (Wasserburg and Depaolo, 1979). However, later studies have clearly shown that this simplistic global process is not the case and/or such mixing is only between enriched OIB sources or their melts and DMM or its melt (e.g., White et al., 1993; Hanan and Schilling, 1997). Moreover, the unified solution is specific to the Pb paradoxes; it does not address other major features of oceanic basalts including the presence of still quite primitive signature of noble gases in OIB and other geochemical variations, such as those, e.g., by Hf and Os isotopes. Although all these are very important and related issues, quite simply they are beyond the scope of this manuscript.

2. An alternative new approach to old Pb paradoxes

The first concept being advocated here is that the paradoxes represent ratios of elements comprising a universal set (i.e., entire mantle) and its individual subsets (i.e., proposed end-member sources of oceanic basalts). These ratios therefore are all interrelated and exhibit features of the set's population. For example, an alternative but, perhaps, overlooked way to express the 2nd paradox is that the mantle sources of oceanic basalts have U/Th ratios higher than that of BSE. This nonconventional expression shows the obvious common feature of the 1st and 2nd paradoxes—the numerator U is higher than both the denominators in U/Pb and U/Th. This, in turn, indicates that both paradoxes can reasonably and simply be solved by a long time-integrated increase of U in the mantle sources of oceanic basalts (Castillo, 2015). Of course, such a solution has already been proposed, such as the preferential recycling of U into the mantle due to oxidizing conditions at the Earth's surface since Early Proterozoic (Staudigel et al., 1995; Elliott et al., 1999; Hofmann, 2003; Andersen et al., 2015). It is important to note, however, that only a few of the preferential recycling of U proposals emphasize the direct connection between long-time integrated enrichment of U in the mantle on the one hand and both 1st and 2nd Pb paradoxes on the other (e.g., Zartman and Haines, 1988; Kramers and Tolstikhin, 1997; Castillo, 2015). In general, it is not the favored solution to the 1st paradox (Murphy et al., 2003; Hofmann, 2003; Hart and Gaetani, 2006; Burton et al., 2012). Moreover, it has never been proposed as part of the solution to the 3rd paradox.

Besides providing a unified solution to the 1st and 2nd paradoxes, a long time-integrated enrichment of U has three additional significant

implications. First, a long time-integrated enrichment of U in the mantle naturally means generation of radiogenic Pb daughter isotopes (Pb*) as well (Castillo, 2015). This is because U is radioactive, the half-life of ^{238}U is comparable to the age of the Earth whereas that of ^{235}U is shorter than the age of the Earth and there is no known geochemical process that can effectively separate ^{206}Pb and ^{207}Pb daughter isotopes from their respective ^{238}U and ^{235}U parent isotopes in the mantle. Thus, addition of U early in the Earth's history to a particular mantle source (e.g., HIMU source) means eventual growth of Pb* as well (Castillo, 2015). Note that the presence of Pb* in individual mantle sources is definitely needed in the first place to explain the observed highly radiogenic Pb isotopes of oceanic basalts (Fig. 1) that, in turn, generate the Pb paradoxes.

Second, the addition of U and, albeit to a lesser extent, Pb (i.e., high U/Pb) is in conflict with the aforementioned proposed explanations for the constancy of Ce/Pb and Nb/U ratios. Addition of U and Pb is inconsistent with the proposed homogeneous mantle source for oceanic basalts with respect to Ce/Pb and Nb/U (Hofmann et al., 1986; Hofmann, 2003). It is also in conflict with the proposed compensatory changes in the incompatible behavior of Ce, Pb and Nb to explain the constancy of Ce/Pb and Nb/U ratios, which are based on partial melting models that require constant concentrations of these elements in the mantle sources of oceanic basalts (Sims and DePaolo, 1997; Hart and Gaetani, 2006). The conflict between the two proposed solutions will be discussed in more detail in Section 3.

Finally, Th/U ratios of all oceanic basalts vary within a limited range. As noted earlier, the κ values of all oceanic basalts vary only from the BSE κ value of ca. 4.0 and DMM value of 2.5 (Galer and O'Nions, 1985; Elliott et al., 1999; Turcotte et al., 2001; Blichert-Toft et al., 2010; Andersen et al., 2015). To a first order, the median κ value of the range is 3.25 ± 0.75, which is within error of the calculated κ value of 3.35 ± 0.1 for the whole mantle by Turcotte et al. (2001); its variance of ± 23% is roughly comparable to the variances of the originally reported constant Ce/Pb (25 ± 5 or 20%) and Nb/U (47 ± 10 or 21%) of oceanic basalts (Hofmann et al., 1986). More specifically, the κ values of MORB calculated from Pb isotope ratios have previously been claimed to be 're-markably homogeneous' (Elliott et al., 1999). This is consistent with the recently constrained mean MORB Th/U of 3.12 ± 0.59 (Table 1—Jenner and O'Neill, 2012; see also Gale et al., 2013), meaning the Th/U of MORB is homogeneous or constant. Note that the aforementioned median κ value of oceanic basalts at 3.25 translates to Th/U = 3.14, which is the same as the MORB Th/U = 3.12 ± 0.59. Thus, the Th/U of MORB, at least, is also constant and the Th/U of the bulk of OIB varies only within

a narrow range, between the constant MORB Th/U of 3.12 and BSE Th/U of 3.88 (Blichert-Toft et al., 2010; Andersen et al., 2015).

Significantly, if Ce/Pb, Nb/U and Th/U in MORB are all constant, and noting that the ratio of two constant values is also constant, then their relationship to U/Pb and to each other can be expressed through the following equations:

$$k_1 = Ce/Pb/Nb/U \tag{1}$$

$$= Ce/Nb * U/Pb \tag{2}$$

$$k_2 = Ce/Pb/Th/U \tag{3}$$

$$= Ce/Th * U/Pb \tag{4}$$

and

$$k_3 = Nb/U/Th/U \tag{5}$$

$$= Nb/Th \tag{6}$$

where k_1 and k_2 have to be the constant values that relate U/Pb to Ce/Nb and Ce/Th ratios, respectively, whereas k_3 is the constant Nb/Th ratio. These relationships may appear trivial and unimportant, but they are part of the body of evidence for the linked features of the ratios or paradoxes. Such a close relationship makes the Pb paradoxes a 'system of equations' that should be dealt with all together or simultaneously, as their solutions need to satisfy every equation in the system.

3. Solving the Pb paradoxes in MORB simultaneously

Mid-ocean ridge basalts, the most voluminous type of oceanic basalts, are produced through adiabatic decompression partial melting of the upper mantle along the ca. 65,000 km long mid-ocean ridge system. Studies have shown that although MORB are relatively more homogeneous than OIB as a whole, they also have highly radiogenic Pb isotopes (Fig. 1) and, hence, posses the concomitant Pb paradoxes as well.

3.1. Constancy of ratios and 3rd Pb paradox in MORB

To solve the 3rd Pb paradox in MORB, the constancy of ratios indicated by Eqs. (1) to (6) is examined first using the mean trace element contents of ocean floor basalts (OFB—Jenner and O'Neill, 2012) and

Table 1
Mean concentrations and ratios of U, Th, Pb, Ce, and Nb in MORB.

	OFB		ALL MORB		OIB	DMM
Ce	13.71 ± 0.88		13.95 ± 0.85		84.9 ± 3.3	0.550 ± 0.099
Pb	0.553 ± 0.035		0.586 ± 0.037		3.73 ± 0.30	0.018 ± 0.003
Nb	6.28 ± 0.78		5.83 ± 0.73		49.6 ± 1.9	0.1485 ± 0.0208
U	0.137 ± 0.018		0.133 ± 0.017		1.14 ± 0.07	0.0032 ± 0.0005
Th	0.429 ± 0.059		0.435 ± 0.057		4.81 ± 0.29	0.0079 ± 0.0011
	m1	m2	m1'	m2'	m3	
Ce/Pb	24.80 ± 2.24	23.69 ± 3.37	23.80 ± 2.09	19.99 ± 5.06	22.69 ± 2.56	
Nb/U	45.69 ± 8.26	42.74 ± 1.62	43.76 ± 7.81	43.30 ± 2.21	43.30 ± 3.12	
Th/U	3.12 ± 0.59	3.25 ± 0.09	3.26 ± 0.60	3.46 ± 0.09	4.21 ± 0.36	
Nb/Th	14.63 ± 2.70	13.13 ± 1.25	13.41 ± 2.44	12.11 ± 2.34	10.29 ± 0.73	
Ce/Nb	2.18 ± 0.31		2.39 ± 0.33			
U/Pb	0.248 ± 0.036		0.227 ± 0.032			
Ce/Th	31.96 ± 4.83		32.09 ± 4.66			
k_1	0.543 ± 0.110		0.544 ± 0.108			
k_2	7.94 ± 1.67		7.29 ± 1.48			
k_3	14.63 ± 3.84		13.41 ± 3.43			

Notes: OFB dataset is from Jenner and O'Neil (2012); ALL MORB dataset includes segment-weighted normal- and enriched-MORB values from Gale et al. (2013). Backarc basin and aseismic ridge samples were removed from both datasets (see Supplementary Data for details). Mean OFB and ALL MORB element values ± 2 sigma uncertainties are averages of elements from each dataset. OIB composition ± 2 sigma uncertainties are means of elements from isotopically extreme HIMU, EM1 and EM2 OIB of Willbold and Stracke (2006, 2010) and Garapic et al. (2015); DMM composition is from average concentrations ± largest spread from the ranges of Workman and Hart (2005)—all in ppm. Element ratios ± 2 sigma uncertainties in sub-columns m1 and m1' were calculated from mean values of individual elements. k_1, k_2 and k_3 ± 2 sigma uncertainties were derived using Eqs. (1), (3) and (5), respectively. Element ratios ± least square errors in sub-column m2 and m2' were calculated through linear regression of individual element pairs. Element ratios in sub-column m3 were calculated from the mixing line between OIB and DMM. Additional discussion is in the text and in Fig. 3.
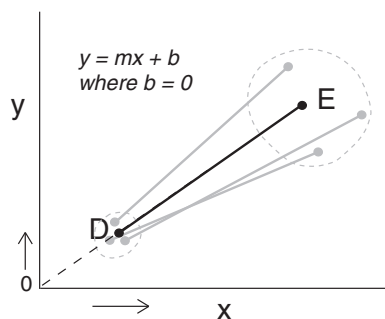
normal- and enriched-MORB (ALL MORB—Gale et al., 2013; Table 1). The former represents high quality analyses of glasses directly coming from the upper mantle determined through modern, inductively-coupled plasma mass spectrometric method whereas the latter is a compilation of modern and previously available analyses of oceanic basalts that were rigorously investigated and grouped to represent various tectonic sections of the mid-ocean ridge system. The mean Ce/Pb (23.80 ± 2.09) and Nb/U (45.69 ± 8.26) of OFB are within the limits of the aforementioned proposed constant or 'canonical' values (25 ± 5 and 47 ± 10, respectively) for oceanic basalts. By substituting these mean values in Eq. (1), $k_1 = 0.543 \pm 0.110$. The product of mean Ce/Nb and U/Pb of OFB is also 0.543 ± 0.110 and this is constant per Eq. (2). Next, the substitution of mean Th/U (3.12 ± 0.59) and Ce/Pb (24.80 ± 2.24) of OFB in Eq. (3) makes $k_2 = 7.94 \pm 1.67$. The product of mean Ce/Th and U/Pb of OFB is also 7.94 ± 1.61 and likewise constant per Eq. (4). Finally, substituting the mean Nb/U (45.69 ± 8.26) and Th/U (3.12 ± 0.59) of OFB in Eq. (5) makes $k_3 = 14.63 \pm 3.84$, which is the same as the mean Nb/Th = 14.63 ± 2.70 of OFB, and this is constant per Eq. 6. It is noteworthy that Gale et al. (2013) originally filtered their ALL MORB dataset for problem samples not having constant Ce/Pb and Nb/U. To avoid circularity of reasoning, errant values are not filtered out in the ALL MORB dataset used here (see notes under Table 1 and Supplementary data). Significantly, the same evaluation used for OFB performed on an unfiltered ALL MORB dataset generates similar results (also in Table 1).

To briefly summarize, like Ce/Pb and Nb/U, the Th/U ratio of MORB coming from the upper mantle is constant at ca. 3.12–3.26 (Table 1). Consequently, the mean Th/U of the bulk of OIB has a narrow range between such a constant MORB value and BSE value of 3.88 (Blichert-Toft et al., 2010; Andersen et al., 2015) or 3.50 ± 0.38. It also follows that the Nb/Th of MORB is constant.

The results of the above exercise beg the questions why are the relationship of U/Pb to Ce/Nb and Ce/Th as well as why are Ce/Pb, Nb/U, Th/U, and Nb/Th constant in MORB and what does 'constant' really mean? The constancy is proposed here to be the result of binary mixing between DMM and a geochemically enriched and heterogeneous mantle component in the form of carbonatitic silicate melt produced by very small degree partial melting of subducted oceanic lithosphere overlain by the relatively more fusible basalt and sediments (Castillo, 2015). The fundamental concept behind this proposal is illustrated through a mixing scenario between two end-components D and E in an element x vs. element y variation diagram (Fig. 2). Such binary mixing generates a straight line that can be expressed simply as

$$y = mx + b \tag{7}$$

where m is the slope of the line and b is its y intercept. Here, m is dependent upon the values of y, x and b. However, when the intercept of the line (or b) is at or close to zero, m simply becomes a function of the ratio of elements x and y, or

$$y/x = m + \sim 0 \tag{8}$$

In the proposed solution, the two end-components D and E are DMM and enriched mantle component, respectively, and E dominates D as D is relatively close to 0. Moreover, the axes are any of Ce (or Nd—Hart and Gaetani, 2006)–Pb, Nb–U, Th–U, or Nb–Th pairs (Fig. 3). As the binary mixing lines between D and E with respect to these element pairs intercept y at or near zero, their observed ratios is simply m and constant.
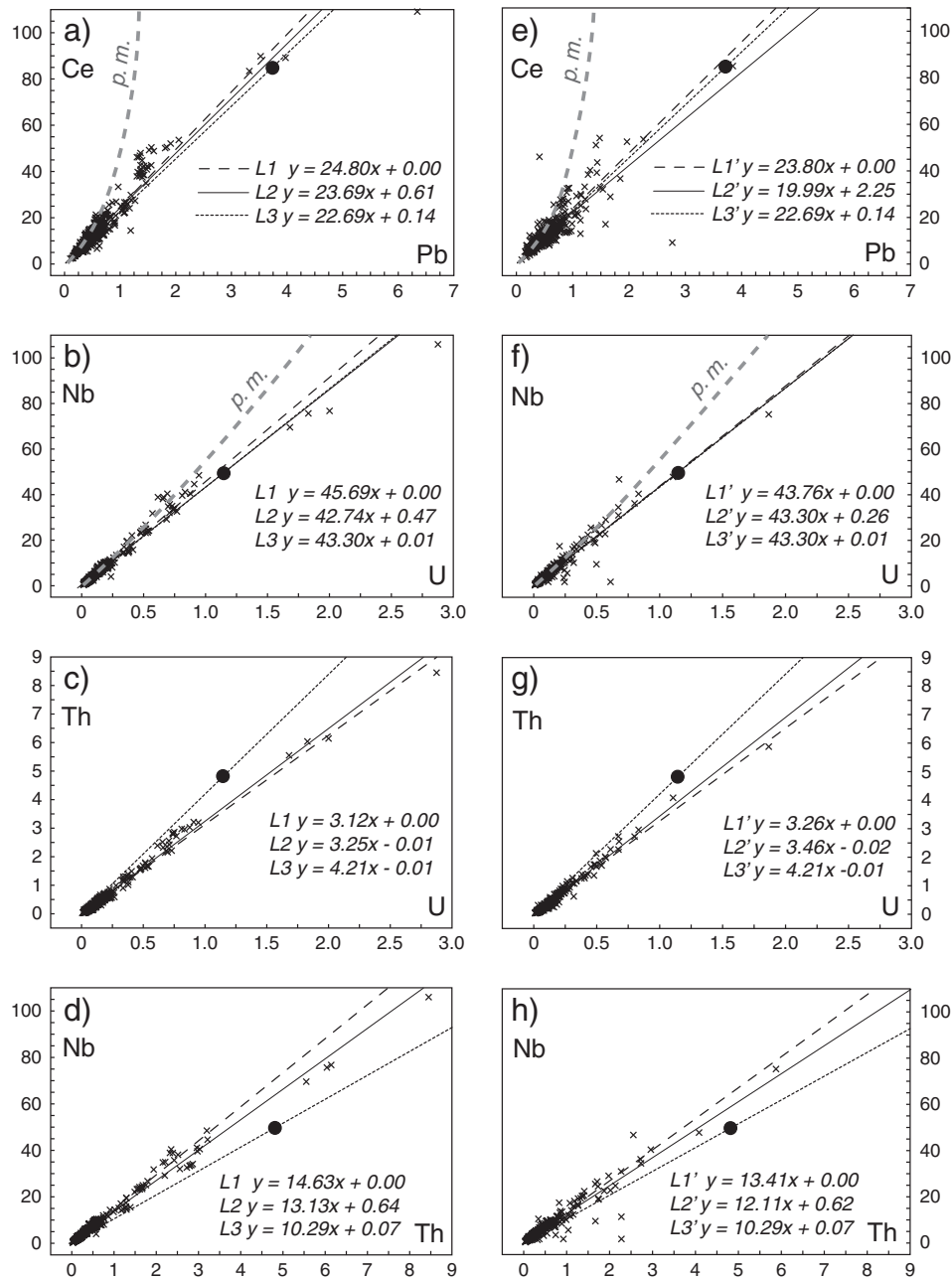
It is noteworthy that the proposed binary mixing will not generate constant ratios for all elements in MORB. This is because typically the two end-components are variably heterogeneous, with the enriched component or carbonatitic silicate melt much more so than DMM. Thus, because element concentrations in the enriched component are typically heterogeneous, the average ratios of two elements have large errors and/or the y-intercepts of their binary mixing lines are not zero (i.e., $b \neq 0$). Another case of $b \neq 0$ is when the slope of the line m approaches zero or infinity because the concentration of at least one of the elements is essentially the same for both end-components. Obviously, no binary mixing array is resolvable (within error) when the end-component melt concentrations are similar, i.e., end-components will simply cluster or plot as a single point.

The proposed binary mixing is also a continuous process and, hence, the observed constant ratios represent averages or means of individual constant ratios during different mixing events that most probably started a long time (b.y.) ago, coinciding with the subduction of oceanic slab or entire oceanic lithosphere into the mantle. Additionally, the proposed mixing can occur between melts coming from DMM and from subducted oceanic lithosphere or between upper mantle peridotite and small pockets of pyroxene-, amphibole- or phlogopite-rich mantle produced through metasomatism by the small degree partial melts (Graham et al., 1988; Niu et al., 2002; Castillo et al., 2010). Thus, it is also being advocated here that the relationships and ratios of U, Th, Pb, Ce (or Nd), and Nb are actually only 'near constant' or vary within a narrower range compared to those of other element pairs in the mantle. For consistency with previous studies, however, the terms constant or canonical values for the elements of concern are retained in the reminder of the discussion.

3.2. Constancy of ratios and 1st and 2nd Pb paradoxes in MORB

The proposed binary mixing to solve the Pb paradoxes in MORB is illustrated further by going into details of the conflict between addition of U and Pb in the mantle source versus the proposed changes in the K_d values of Ce and Nb that are different from those inferred from experimental results (Sims and DePaolo, 1997; Hart and Gaetani, 2006), as mentioned earlier. The latter proposal approached the constancy of Ce/Pb and Nb/U ratios through partial melting models of the mantle source. In the case for MORB, the constancy of Ce/Pb is commonly described as too much Ce for given Pb with decreasing degree of partial melting of the normal, peridotitic upper mantle (Fig. 3a and e). The dilemma is solved by assigning a larger K_d for Pb (Sims and DePaolo, 1997; Hart and Gaetani, 2006) than predicted by experimental results. However, although this approach gives mathematically sound solutions, it does not simultaneously explain the range of radiogenic Pb isotopic ratios of MORB (Fig. 1). Moreover, although the proposed compensatory change in the K_d for Pb is able to explain the 1st paradox (Hart and Gaetani, 2006), it cannot simultaneously solve the 2nd paradox and constant Nb/U (cf., Sims and DePaolo, 1997).

The proposed binary mixing scenario posits addition of carbonatitic silicate melts enriched in Pb ($Pb_{recycled} + Pb^*$) and $Ce_{recycled}$ to DMM and

Fig. 2. An x vs. y diagram containing components D and E. Mixing between the components generates a straight line. In the proposed model, the binary mixing line intersects the y-axis at or near zero. The black dots and line represent average values while the gray dots and lines represent individual mixing events. See text for discussion.

Fig. 3. Mean Ce vs. Pb (a) and (e), Nb vs. U (b) and (f), Th vs. U (c) and (g), and Nb vs. Th (d) and (h) plots for OFB (Jenner and O'Neill, 2012) and ALL MORB (Gale et al., 2013). See Data supplement for more information. Thick dash curves in (a), (b), (e), and (f) labeled p.m. represent equilibrium batch partial melting curves for a spinel lherzolite and/or garnet–lherzolite source (Sims and DePaolo, 1997). The large black dot in each figure is the enriched component or average composition of OIB with extreme isotopic values (from Table 1). See text for discussion.

such addition has the following features. (1) Addition of Pb* from carbonatitic silicate melts to unradiogenic Pb in DMM generates the radiogenic Pb isotopic composition of MORB (Fig. 1). (2) Presence of Pb* means presence of an even higher amount of its radioactive parent U (i.e., high U/Pb and U/Th), which explains both 1st and 2nd paradoxes. (3) Adding both Pb and Ce to DMM produces the observed constant Ce/Pb ratio in MORB without invalidating the experimental K_d values for both Ce and Pb (Figs. 2, 3a and e). Note that the observed constant value is the slope of the line ($m \sim 25$) that intercepts the axes at or close to zero ($b \sim 0$).

The same line of reasoning holds true for the proposed binary mixing explanation for the constancy of Nb/U. Adding carbonatitic silicate melts enriched in $U_{recycled}$ and $Nb_{recycled}$ to DMM can also explain both the 1st and 2nd paradoxes, adds daughter Pb* to generate the radiogenic Pb

isotopic composition of MORB (Fig. 1) and creates the observed constant Nb/U of MORB without invalidating the experimental K_d values for both U and Nb (Figs. 2, 3b and f; $m \sim 45$; $b \sim 0$). Where does Nb come from? Carbonatitic silicate melts are small-degree partial melts from subducted oceanic lithosphere that carries the residual geochemical signature of subduction zone magmatic processes. Thus, arc lavas and OIB should possess some compensatory geochemical features (Castillo, 2015). For example, the distinctive Pb enrichment in arc lavas is counterbalanced by Pb depletion in oceanic basalts. More relevant to the present study is the hallmark depletion in some HFSE, particularly Nb, in arc lavas is counterbalanced by enrichment of these elements, or positive 'TITAN anomalies' (Jackson et al., 2008) that are pervasive in OIB (Peters and Day, 2014). What is also being advocated here is that although carbonatitic silicate melts have the bulk

compositional signature of subducted lithosphere, they may not necessarily display some of the geochemical features of primitive carbonatite melts (e.g., Nb depletion—Walter et al., 2008). This is because the latter act primarily as dirty 'melt flux' and 'radiogenic Pb isotope spike'; this notion will be discussed in more detail in Section 4.

That the proposed recycling of crustal U in the upper mantle most likely surged during the last 600 m.y. (Castillo, 2015) is highly consistent with the presence in MORB of isotopically distinct, high $^{238}U/^{235}U$ ratios (Andersen et al., 2015). These 'exotic' $^{238}U/^{235}U$ ratios are formed at the bottom of an oxic ocean and carried by the oceanic crust subducting into the mantle. Notably, however, the recycling or return of some of such exotic, crustal ratios from the upper mantle back to the surface has to be way beyond the arc front (cf., Andersen et al., 2015) because the $^{206}Pb/^{204}Pb$ ratios of MORB can be as high as ca. 20.0 (see also, Hanan and Graham, 1996) and the $^{207}Pb/^{206}Pb$ slope of MORB forms an apparent secondary isochron with a 1.5 Ga age (Fig. 1a). As argued earlier, U and Pb in the mantle are interrelated parts of a universal set or system of equations and, thus, the inventory of radioactive U in the upper mantle is tied to the Pb isotopic composition of the upper mantle. In other words, some of the recycled U have to be old enough to be accompanied by daughter Pb* that can account for the radiogenic signature of some MORB. Residual Pb that comes together with exotic $^{238}U/^{235}U$ in the subducted oceanic crust beyond the arc front (Andersen et al., 2015) has high $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ for a given $^{206}Pb/^{204}Pb$ and, thus, cannot account for the radiogenic $^{206}Pb/^{204}Pb$ of modern MORB.

In summary, the observed Ce/Pb, Nb/U, Th/U, and Nb/Th in MORB are most likely the results of binary mixing between DMM and enriched, carbonatitic silicate melts coming from recycled oceanic lithosphere. Despite the heterogeneity of the enriched component, its average Ce/Pb, Nb/U, Th/U, and Nb/Th ratios vary within a limited range and the binary mixtures they form with DMM appear constant because in general their mixing lines intercept the y-axis at or close to zero. The mixing process is illustrated using both OFB (Fig. 3a–d) and ALL MORB (Fig. 3e–h) datasets (see also Table 1). The enriched component is compositionally akin to OIB as they share a common source. The slopes of the binary mixing lines (L1–L1', L2–L2' and L3) were respectively determined in three ways: (m1–m1') ratios of mean values of individual elements ±2 sigma uncertainties in the two datasets, (m2–m2') linear regression of individual element pairs ± least-square uncertainties and (m3) through mixing between DMM (Workman and Hart, 2005) and an enriched OIB component derived from the mean concentrations of the isotopically most extreme OIB from HIMU, EM1 and EM2 type localities (Willbold and Stracke, 2006, 2010) and most recent data for Pitcairn (Garapic et al., 2015) ±2 sigma uncertainties. As Willbold and Stracke (2006, 2010) have proposed, the parental magmas for this OIB component originate mainly (ca. 90%) from the lithospheric mantle of the subducted slab and the remainder (ca. 10%) from variable proportions of different types of recycled crust. Notably, the composition of the enriched OIB component here is similar to the OIB composition proposed by Sun and McDonough (1989). Mixing of DMM and enriched component produces slopes (m's) of mixing lines (L's) that are basically the same and y intercepts (b's) close to zero given the uncertainties associated with m's in all calculations (Table 1) and the effects of partial melting, fractional crystallization, and seafloor alteration on element concentrations that are not factored in the calculations. Significantly, the m's in Ce vs. Pb (Fig. 3a and e) and Nb vs. U (Fig. 3b and f) diagrams are the respective canonical Ce/Pb (~25) and Nb/U (~47) of oceanic basalts (Hofmann et al., 1986; Hofmann, 2003).

It is important to note that although recycled marine carbonates are being advocated here as crucial to generate OIB magmas, again these are mainly considered as melt flux and radiogenic Pb isotope spike in the OIB generation process. Carbonatite magmas are produced through pooling of extremely small volume carbonate melts exsolved from carbonated peridotite and eclogite (e.g., Dasgupta et al., 2006). Thus, they have extremely heterogeneous compositions (e.g., Hoernle et al.,

2002; Bizimis et al., 2003) and do not have the appropriate enriched composition.

It is also important to clarify that the marine carbonate recycling hypothesis posits that some fragments of limestone, with μ's higher than that of the BSE (i.e., μ's > ~9), are being subducted (Castillo, 2015). This is highly consistent with the absence or near absence of arc volcanism at, e.g., 1) the boundary between Izu-Bonin and Marianas arcs, 2) the boundary between Tonga and Kermadec arcs, and 3) the segment of the Central American volcanic arc in the Costa Rica–Panama region where the Ogasawara Plateau, Louisville Seamount Chain and Cocos Ridge, respectively, are subducting. These tectonic features are all capped with limestone and so are the numerous seamounts, atolls and guyots in the western Pacific that will eventually be subducted. Significantly, these pure limestone fragments are not included in the global subducting sediment (GLOSS) compilation that has generally low, but highly variable μ's (2.9 to 12.8; Plank and Langmuir, 1998). This is because GLOSS consists of subducting sediments that would potentially be involved in arc magma generation (Plank and Langmuir, 1998) whereas the limestone capping of massive seamounts and plateaus being subducted escapes the early phase, at least, of arc magma generation.

4. A unified solution to the Pb paradoxes

4.1. A conceptual model for the trace element evolution of the upper mantle

The process of mixing or adding the enriched component to DMM is schematically shown in Fig. 4. Recent experimental results and inferences from these indicate that partial melting starts at a very small degree and deep in the upper mantle due to the presence of CO_2 (Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013). Significantly, the presence of small volume partial melts in the deep upper mantle is evidently shown by high electrical conductive zone at >150 km depth (Lizarralde et al., 1995; Key et al., 2013). It is being advocated here that the flux melting effect of CO_2 represents the egress of small amounts of carbonatitic silicate melts from marine carbonates in the subducted oceanic lithosphere stored either in the transition zone or in the lower mantle (Castillo, 2015). The process returns small-volume, compositionally heterogeneous alkalic partial melts enriched in CO_2, Ca, U, Pb (+Pb*), Th, Ce, Nb, and other residues in the subducted oceanic lithosphere after magma genesis along subduction zones to the upper mantle. A most significant feature of the additional Pb* is that it is both variable in amount and isotopically radiogenic ($^{206}Pb/^{204}Pb$ up to ca. 20.0—Fig. 1; see also Hanan and Graham, 1996). Moreover, DMM can be easily contaminated because to begin with it has low Pb content (0.018 ppm) and is relatively unradiogenic (i.e., $^{206}Pb/^{204}Pb$ down to 17.57—Workman and Hart, 2005). In other words, Pb is indeed low in the upper mantle (and other proposed sources of oceanic basalts) most likely due to its hydrothermal transfer to continental crust (Peucker-Ehrenbrink et al., 1994; Chauvel et al., 1995; Hofmann, 2003) and/or its storage in residual mantle sulfide (Hofmann, 2003; Hart and Gaetani, 2006; Burton et al., 2012). Such Pb depletion is clearly observed as a negative Pb anomaly in normalized trace element concentration diagrams. Although Pb depletion plays some role in generating the long-time integrated high U/Pb (e.g., Chauvel et al., 1995; Hofmann, 2003; Hart and Gaetani, 2006; Burton et al., 2012), its main relevance to the Pb paradoxes is that it makes DMM (and OIB sources) highly susceptible to contamination by the highly radiogenic Pb* from *in situ* decay of recycled U in the subducted marine carbonates. That is, spiking the small inventory of Pb in the mantle with a miniscule amount of such Pb* produces the highly radiogenic Pb isotopic ratios of oceanic basalts (Fig. 1).

As noted earlier, carbonatitic silicate melts comprise the small-volume, geochemically enriched alkalic melts that infiltrate the upper mantle from below and/or form the enriched, more fusible metasomatic phases such as pyroxenes, amphiboles and phlogopite. These phases, in turn, most likely are partly responsible for the 'marble cake' (Allegre and
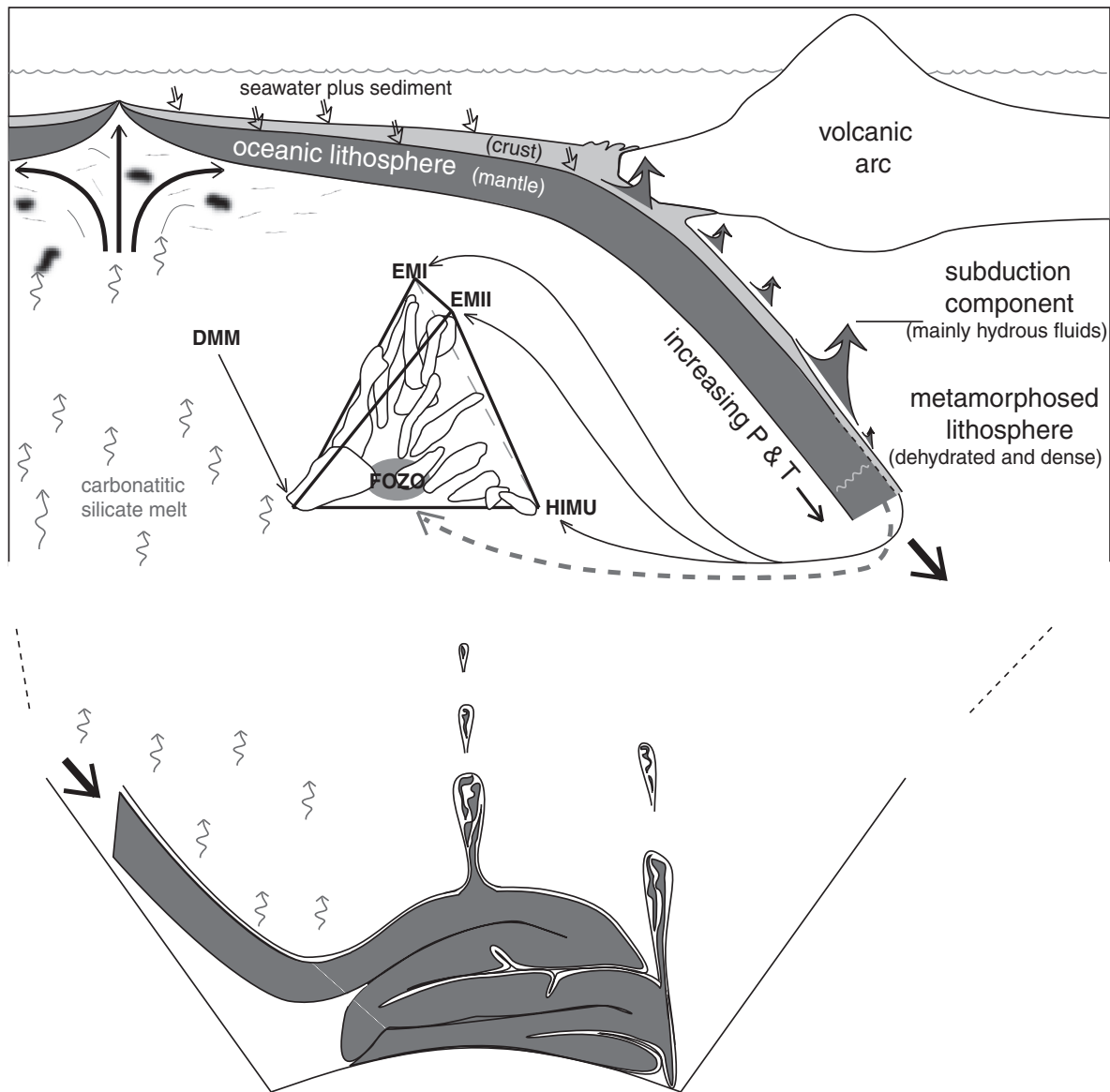
Fig. 4. A conceptual model for the trace element evolution of the upper mantle source of MORB and deeper mantle sources of OIB (modified from Castillo, 2015). In the upper mantle, binary mixing occurs between enriched, carbonatitic silicate melts derived mainly from the crustal portion of previously subducted oceanic lithosphere and DMM. In OIB sources, binary mixing occurs between enriched HIMU and EM1, EM2 mantle sources, also mainly derived from the crustal portion, and FOZO, which is the mantle portion, of previously subducted oceanic lithosphere. See text for discussion.

Turcotte, 1986) or 'plum pudding' (Hanson, 1977) fabric of the upper mantle and are preferentially sampled during small-degree partial melting (Graham et al., 1988; Niu et al., 2002; Castillo et al., 2010). Geochemical enrichment comes from small degree partial melting of the variably enriched crustal portion of subducted oceanic lithosphere. Specifically, the alkalic melts or metasomatized phases have higher contents of incompatible trace elements (e.g., U, Pb (+Pb*), Th, Ce, Nb) and higher U/[Pb (+Pb*)] than DMM. Their mixing with DMM can simultaneously explain the radiogenic Pb isotopic ratios (Fig. 1), uncharacteristically high U/Pb (1st Pb paradox), low Th/U (2nd Pb paradox), and constant Ce/Pb, Nb/U, Th/U, and Nb/Th (3rd Pb paradox) of MORB.

4.2. A conceptual model for the trace element evolution of the mantle sources of OIB

The proposed solution to the Pb paradoxes in MORB (Figs. 2 and 3) is clearly inconsistent with many of the proposed satisfactory solutions to the Pb paradoxes in OIB mantle sources mentioned in Section 1. The same basic argument, however, was used as a solution to the 1st and 2nd Pb paradoxes in the HIMU basalts and the bulk of OIB (i.e., those classified as young HIMU or FOZO) by the recently proposed marine carbonate recycling hypothesis (Castillo, 2015). The hypothesis posits that marine carbonates are a natural source of HIMU isotopic signature because they initially contain U but negligible Pb. After subduction, storage and partial melting deep in the mantle, these carbonates also contain *in situ*-generated daughter Pb*. Thus, old recycled marine carbonates are a natural radiogenic Pb isotope spike, albeit a dirty one; they are also a melt flux as they promote melting or lower the mantle solidus (Dasgupta et al., 2013; Rohrbach and Schmidt, 2011; and references therein). The resultant enriched melt is compositionally much more heterogeneous than DMM because of the highly variable composition of the subducting oceanic lithosphere. In any case, together with high Sr but negligible Rb contents, a small amount (few %) of Archaean marine carbonates in the subducted oceanic lithosphere is enough to provide the distinct $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{87}Sr/^{86}Sr$, U/Pb, Th/U, and major-trace element compositions of classic HIMU, whereas post-Archaean marine carbonates provide similar distinctive

compositions of FOZO basalts. Thus, the addition of recycled marine carbonates enriched in U and Pb* (or dirty spike) to the common source of OIB (see details below) offers a possible common solution to the 1st and 2nd Pb paradoxes in HIMU and FOZO (or bulk OIB), similar to the solution proposed above for MORB. The major question is can marine carbonate recycling also explain the 3rd Pb paradox in OIB?

Mixing of sources and/or melts is a common feature of OIB and/or their mantle sources (Hart et al., 1992; Hofmann, 2003; Stracke, 2012; and references therein). This is clearly illustrated by the curvilinear to linear arrays in the plots of geochemical and isotopic data for OIB. However, mixing between EM1, EM2 and HIMU is rare (Hart et al., 1992; Jackson et al., 2014). More common is mixing between individual end-members and a depleted mantle component. More relevant to this study is that a less enriched or a variably depleted component is intrinsic to the source of OIB and OIB-like lavas as shown for the Marquesas (Castillo et al., 2007), Iceland (Fitton et al., 1997), Hawaii (Frey et al., 2005), Cretaceous Caribbean–Colombian oceanic plateau (Kerr et al., 2002), and the East African rift system (Castillo et al., 2014).

In the proposed marine carbonate recycling hypothesis (Castillo, 2015), the intrinsic, variably depleted, ultramafic component in OIB sources comes from the mantle portion of the subducted lithosphere, or what is commonly referred to as FOZO (Fig. 4). The young HIMU signature mentioned earlier is the typical, variable and radiogenic Pb isotopic composition of FOZO. The hypothesis posits that FOZO is isotopically depleted because 1) of prior extraction of MORB from the lithospheric mantle, which means FOZO comes from the uppermost depleted portion of the mantle at any given time, and 2) dehydration plus partial melting (or selective geochemical cleansing) processes at subduction zones remove many fluid-mobile incompatible trace elements from subducting lithosphere. Upon later partial melting deep in the mantle, fluxed by CO_2 (Rohrbach and Schmidt, 2011; and references therein) from subducted marine carbonates, this ubiquitous ultramafic portion of the lithosphere provides the common basaltic foundation of OIB. Enriched mantle 1, EM2 and HIMU end-members add flavors to FOZO, extending OIB compositions to extreme, distinct compositions. Conversely, individual OIB end-members are 'fan-shaped and appear to converge on' FOZO (Hart et al., 1992). Either way, end-members are connected to FOZO through mixing. Thus, similar to MORB, the bulk of OIB is generated through binary mixing between enriched (EM1, EM2, HIMU) and relatively depleted (FOZO) mantle components and this is the reason why OIB also possess the 3rd Pb paradox. Recycling of marine carbonates, which carry U and Pb* from subducted lithosphere, offers a process to generate such a unified solution to the Pb paradoxes in both MORB and OIB sources.

Finally, the proposed unified solution does not require a unique 'low μ' reservoir, which is required to complement many of the proposed solutions to the 1st paradox (e.g., Murphy et al., 2003; Hofmann, 2003; Burton et al., 2012). This is because the radiogenic Pb isotopic signature and concomitant 1st Pb paradox of oceanic basalts are due to addition of Pb*, or are a HIMU effect (Vidal, 1992; Stracke et al., 2005; Castillo, 2015). As the addition of dirty Pb* spike is mainly responsible to drive the Pb isotopic composition of oceanic basalts to the right of the geochron (Fig. 1), the bulk of the mantle source of oceanic basalts has 'normal' Pb isotopic composition that plots to the left (e.g., the bulk of mantle and old continental rocks) or along (e.g., normal-MORB) the geochron. In the proposed solution, the high μ source component, or dirty Pb* isotopic spike, is manufactured by marine carbonates that take in U, but very little amount of Pb from seawater. Uranium in seawater is derived from continental crust and, to a first order, uniformly distributed since the Proterozoic (Elliott et al., 1999; Andersen et al., 2015) because it has a residence time of ca. 400×10^3 years, longer than the ~1000 years mixing time of the oceans (Sleep et al., 2012). Because marine carbonates thrive in shallow ocean away from active continental runoff and much of subducted U returns to continents via arc magmatism and to upper mantle (Andersen et al., 2015), the manufacturing of high μ marine carbonates does not leave behind any particular low μ reservoir.

5. Summary and conclusions

1) The radiogenic Pb isotopic signature of oceanic basalts requires mantle sources with long-time integrated U/Pb and U/Th unexpectedly higher than those of the primitive mantle or BSE. The mantle sources also have unexpectedly constant Ce/Pb, Nb/U, Th/U, and Nb/Th ratios. These unexpected trace element ratios are termed Pb paradoxes.

2) Studies to solve the Pb paradoxes in the last four decades or so were generally done separately and, thus, have produced highly satisfactory but individualized results.

3) A simultaneous approach to the paradoxes is proposed because the radiogenic Pb isotopes and concomitant paradoxes are very much interrelated as they involve the same set of elements in the mantle and have many common geochemical features. The radiogenic Pb isotopic signature and paradoxes in oceanic basalts comprise a system of equations that must be solved all together as they require solutions that must satisfy all equations in the system.

4) The new simultaneous approach indicates a linear solution to explain the radiogenic Pb isotopic composition and paradoxes in MORB in the form of binary mixing between DMM and enriched, compositionally heterogeneous mantle component mainly coming from the crustal potion of the subducted oceanic lithosphere.

5) Binary mixing between FOZO, the variably depleted, common component in OIB sources, and enriched EM1, EM2 and HIMU sources can also explain the radiogenic Pb isotopic composition and paradoxes in OIB.

6) The process of recycling a small amount of ancient marine carbonates that have intrinsic high μ composition can generate the unified, binary mixing solution to the system of Pb equations in oceanic basalts.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.lithos.2016.02.015.

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