Size and composition of the MORB+OIB mantle reservoir

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Key Points:

- A new assessment of the depleted mantle mass (> 65%) based on (Nb,Ta)/U conflicts with conventional estimates using Nd isotopes (<50%)
- This invalidates the classic 3-reservoir silicate Earth (continental crust, depleted mantle, and primitive mantle).
- The observable, present-day mantle was permanently depleted by segregation or loss of an early-enriched reservoir.

Abstract

Most efforts to characterize the size and composition of the mantle that complements the continental crust have assumed that the mid-ocean ridge basalt (MORB) source is the incompatible-element depleted residue of continental crust extraction. The use of Nd isotopes to model this process led to the conclusion that the "depleted MORB reservoir" is confined to the upper ~30% of the mantle, leaving the lower mantle in a more "primitive" state. Here we use Nb/U and Ta/U to evaluate mass and composition of the mantle reservoir residual to continent extraction and find that it exceeds 67% of the total mantle. Thus the (Nb,Ta)/U-based mass balance conflicts with the ε(Nd)-based mass balance, ~~and~~ this invalidates the classical 3-reservoir silicate Earth model (continental crust, depleted mantle, primitive mantle). Including the combined MORB + ocean island basalt (OIB) sources in the ε(Nd)-based mass balance does not reconcile the conflict as it would require their average ε(Nd) to be ≤3.0, much lower than observed MORB+OIB ε(Nd) averages. We resolve this conflict by invoking an additional, "early-enriched reservoir" (EER), formed prior to extraction of significant continental crust, but now hidden or lost. This EER differs from EERs previously invoked by having no Nb-Ta anomaly. We suggest that it originated as an early mafic crust, which had unfractionated (Nb,Ta)/U but fractionated Sm/Nd ratios. The corresponding "early-depleted" reservoir (EDR) generated the present-day continental crust and the "residual mantle" MORB-OIB reservoir, which occupies at least 70% of the present-day mantle and is only moderately depleted in incompatible trace elements.

Plain Language Summary

The Earth's continental crust makes up only about half a percent of Earth's mass, but it contains a large portion of its total budget of uranium and thorium, which produce much of Earth's interior heat. In making the crust, these elements have been extracted via melts and volcanism from Earth's mantle. But what portion of the mantle was involved in making the continents? Previously, geochemists concluded that only its uppermost 30% was involved, leaving the lower two-thirds of the mantle essentially untouched. The measure used for this estimate has been the difference in the isotope ratios of neodymium, 143Nd/144Nd, between crust and mantle. However, when we use an alternative measure for the same calculation, namely the ratio of niobium to uranium, Nb/U, we find the depleted mantle fraction to be greater than 60%. We therefore need an Earth model that involves an additional "reservoir" with crust-like Nd isotopes but mantle-like Nb/U. We model this as an early Earth ocean crust, which may have been lost to space, or may now be hidden at the base of the mantle. A buried ancient ocean crust might well explain the large density/temperature anomalies recently discovered at the base of the mantle by seismologists.

1 Introduction

The upper portion of Earth's mantle is extensively sampled by mid-ocean ridge basalts (MORBs), and its composition has been estimated using isotope-based modeling and partial melting theory. Most efforts to characterize the size and composition have assumed that the MORB source is the incompatible-trace-element depleted residue of continental crust extraction. The use of Nd isotopes to make this estimate consistently led to the conclusion that the "depleted MORB reservoir" is approximately ~30% of the mantle, which is the approximate size of the upper mantle above the 670 km seismic discontinuity (e.g. Jacobsen and Wasserburg, 1979; O'Nions et al.

1979; DePaolo, 1980; Allègre et al., 1980; Davies, 1981). This further led to the classical three-layer (continents, upper mantle, lower mantle) Earth model, whereby the upper mantle is the MORB source and the lower mantle is left in a more or less "primitive" or "primordial" (i.e. undifferentiated) state. This model was supported by many observations, three important ones are that the lower mantle is sampled by ocean island basalts (OIBs) and oceanic plateaus, at least some of which are generated by deep-mantle plumes (e.g. French and Romanowicz, 2015); early Nd isotope studies of OIB showed values between MORB and chondrites (DePaolo and Wasserburg, 1976; O'Nions et al., 1977); and some of these OIBs contained high $^{3}He/^{4}He$ ratios compared to MORB, confirming their primordial heritage (e.g. Farley et al., 1992).

While these early Nd isotope studies suggested that OIBs were derived from primitive lower mantle, no OIB source has been shown to be truly primitive, and some authors concluded that the less depleted, but non-primitive Nd-Sr isotopic signatures of OIBs are caused by mixing of primitive material from the lower mantle with depleted material from the upper mantle during plume ascent (e.g. Wasserburg and DePaolo, 1979). The combination of deep subduction and rising mantle plumes provide mechanisms for mixing upper and lower mantle, but the differences between the Nd, Hf, and Sr isotopic compositions of OIBs and MORBs indicate that some stratification is preserved in spite of such convective mixing. These isotopic compositions show that MORB sources have been generally more depleted in incompatible trace elements over geological time than OIB sources. Much of this mixing was thought to occur when a rising plume entrains the overlying mantle material (e.g. Hart et al., 1992; Hauri et al. 1994; Farley et al., 1992), but Farnetani and Richards (1995) examined the entrainment process required for such mixing; they found that the entrained material does not significantly contribute to the melts formed by a plume that rises from the deep mantle.

A consequence of the classical three-reservoir (continents, MORB-mantle, primitive mantle) concept for the Earth is that the currently most widely used models for the composition of the depleted MORB-source upper mantle (Salters and Stracke, 2004; Workman and Hart, 2005), though different in some important details, both rely on the basic assumption that the Sm/Nd ratio of this depleted mantle can be derived from its Nd isotopic composition via simple crustal extraction models. In both cases, this crustal extraction is modeled in terms of crustal growth through unidirectional, mantle-to-crust extraction of crustal elements through time. But any simple relationship between parent-daughter ratio and radiogenic enrichment of the daughter element is lost if the actual crustal history was not one of simple unidirectional growth but involved substantial recycling of crust back into the mantle. Moreover, it was shown by Hofmann et al. (1986) and by Campbell (2002) that the continental crust is not the only chemical complement of the depleted mantle, but that stored oceanic crust also contributes a significant portion to the fractionation of Sm/Nd. These considerations cast doubts on the validity of the estimates of the depleted-mantle composition based on mass balance between the continents and the MORB-mantle, and they call for a re-examination of Earth's continent-mantle mass balance. A major point of the present contribution will be to show that the above approach has led to a serious underestimate of the mass of the mantle that is residual to continental extraction, and a corresponding overestimate of its degree of depletion. We employ a simple mass balance approach, using alternatively ε(Nd) and (Nb,Ta)/U in a three reservoir silicate Earth (continental crust, a depleted reservoir that may take into account OIB- as well as MORB-mantle, primitive mantle) to show that the results from the ε(Nd) based mass balance and from the (Nb,Ta)/U based mass balance cannot be reconciled, unless the Earth is either non-chondritic or contains an additional, hidden, enriched reservoir.

The idea of an additional, permanently hidden silicate reservoir, presumably located at the base of the mantle, was introduced by Tolstikhin and Hofmann (2005) on the basis of xenon isotopes, and by Boyet and Carlson (2005) on the basis of their discovery of the non-chondritic terrestrial ratio of $^{142}Nd/^{144}Nd$, reflecting the decay of the extinct nuclide ^{146}Sm. Super-chondritic $^{142}Nd/^{144}Nd$ ratios observed in both crustal and mantle rocks implied that the "accessible silicate Earth" has a superchondritic Sm/Nd ratio, which would be balanced by a subchondritic Sm/Nd located in an inaccessible Early Enriched Reservoir (EER) (Boyet and Carlson, 2005, 2006; Carlson and Boyet, 2008). More recent research has shown that the ^{142}Nd-isotopic compositions of chondrites are variable and do not necessarily require a non-chondritic terrestrial Sm/Nd ratio (e.g. Burkhardt et al., 2016). We will nevertheless adopt Boyet and Carlson's nomenclature of an Early Enriched Reservoir (EER), leaving behind an Early Depleted Reservoir (EDR), because it can reconcile our two independent mass balances for the crust-mantle system. We note, however, that our method for estimating the compositions of these reservoirs is quite different from that employed by Boyet and Carlson (2005); (see also Supporting Information).

Using the mass balance approach originally set out by Davies (1981), we will demonstrate that the traditional three-reservoir silicate Earth (continental crust, depleted mantle, primitive mantle) yields irreconcilable results for the mass balances employing (Nb,Ta)/U and ε(Nd), respectively. We then show that simple differentiation of the depleted mantle into an even-more-depleted MORB source and a less depleted OIB source does not resolve the discrepancy. Finally, we propose a 4-reservoir model including a hidden, early-enriched reservoir somewhat similar, but not identical, to the EER proposed by Boyet and Carlson (2005, 2006) and Carlson and Boyet (2008), or the reservoir lost by accretional erosion postulated by O'Neill and Palme (2008) and Jackson and Jellinek (2013). The complementary early-depleted reservoir (EDR) will be subsequently differentiated into the continental crust and its mantle residue, which we will call the "residual mantle" (RM), in order to distinguish it from the "depleted mantle" (DM) associated with the three reservoir Earth. We show that this residual mantle occupies more than 70% of the total mantle, and its incompatible trace element budget is only moderately depleted.

We use the following terms and symbols to describe the various terrestrial silicate "reservoirs" evaluated by our mass balances:

CC - Bulk continental crust;

PM - Primitive mantle (equal to BSE = Bulk Silicate Earth);

DM - Depleted mantle reservoir in a 3-reservoir Earth, the product of extraction of CC from PM; DM should be capable of generating MORB or MORB+OIB;

EER - Early-enriched reservoir, either permanently stored in the deep mantle or possibly lost by collisional/accretion erosion;

EDR - Early-depleted reservoir = mantle after removal of EER but prior to extraction of permanent continental crust;

RM - Residual mantle reservoir in a 4-reservoir Earth consisting of PM, EER, EDR, and CC. RM is formed by extraction of CC from EDR.

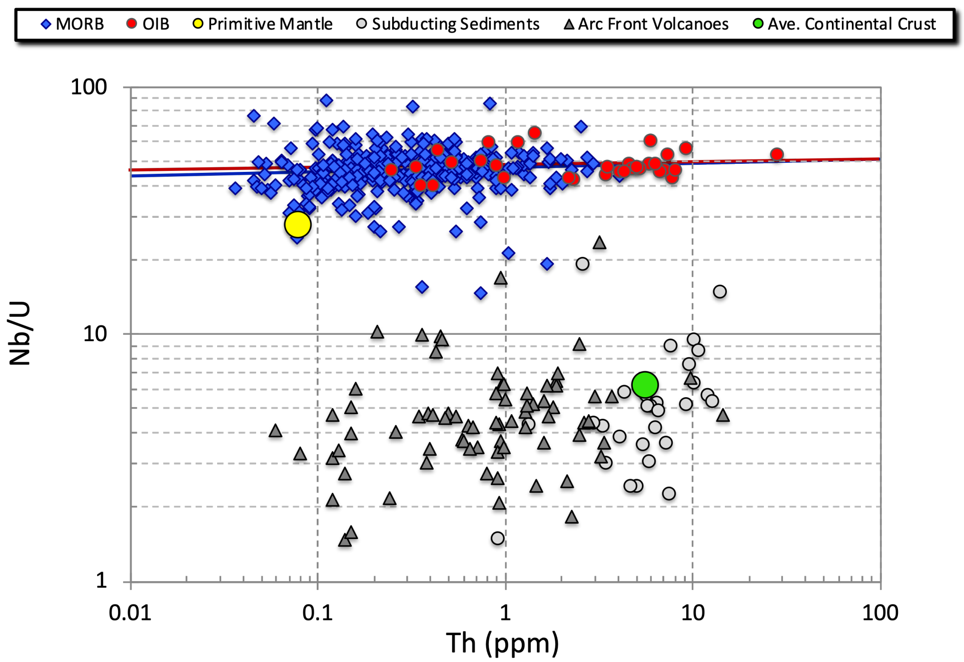


Fig. 1. Nb/U vs. Th for mid-ocean ridge basalts (MORB), oceanic basaltic plateaus, and ocean island basalts (OIB), using MOR segment averages of Gale et al. (2013), average continental crust (Rudnick & Gao, 2003), primitive mantle (McDonough & Sun, 1995), average values for arc front volcanoes (Turner & Langmuir, 2015), and subducting sediments (Plank, 2014). Thorium concentrations are used as a proxy for overall incompatible-element enrichment/depletion. The primitive mantle (McDonough & Sun, 1995) is shown with a reduced Nb value of 0.555 ppm, instead of the value of Nb = 0.658 recommended by McDonough and Sun (1995). The reduced Nb is chosen to account for the loss of Nb from the bulk silicate Earth compared to chondrites (discussed in the section on reassessment of the Nb-Ta-Th-U relationships in oceanic basalts). The data for oceanic plateaus and OIBs were compiled from the GEOROC database (georoc.mpch-mainz.gwdg.de/), and filtered for evidence for U alteration using Th/U ratios (discussed in Supporting Information). The blue and red lines are regression curves for MORB and OIB data, respectively.

2. Data assessment

2.1. Reassessment of the Nb-Ta-Th-U relationships in oceanic basalts

Figure 1 is an update of Figure 1 of Hofmann et al. (1986) that showed Nb/U versus Nb concentrations. It illustrates the relationship of Nb/U between global MORB (Gale et al. 2013), a new compilation of OIB data (Supporting Information Table S1), the continental average of Rudnick and Gao (2003), arc front volcano averages of Turner et al. (2015), subducting sediment averages of Plank (2014), and the primitive mantle value of McDonough and Sun (1995). Thorium concentrations are used as proxies for overall incompatible-element enrichment/depletion. Th in the abscissa rather than Nb avoids using the same variable in both coordinates, a potential problem pointed out by Sims and DePaolo (1997). The original version in Hofmann et al. (1986) was based on only 30 MORB samples and 41 individual OIB samples from 12 ocean island groups. In contrast, Figure 1 represents 260 global MOR segment averages, excluding segments from back arc basins, presented by Gale et al. (2013), in addition to 30 OIB averages representing individual hotspots and seamount chains, as well as 7 oceanic plateau averages, encompassing a total of nearly 4000 rock samples. A truly global assessment of Nb/U of OIBs is still problematic, partly because there is no obvious way to obtain a globally representative sampling of OIBs and their sources. In addition, many U data of OIBs are seriously compromised by alteration. The latter problem can be recognized, and to some extent corrected for, by comparing the Nb/U ratios with Th/U ratios of the same samples. Given the observation that all fresh OIBs have Th/U ratios between 3 and 5, close to the chondritic value of Th/U = 3.8, this has been used to screen most of the data (except those from historical eruptions; see Table S1). Preference has therefore been given to historical eruptions, where fresh samples are readily available. Finally, oversampling of individual OIB can be avoided by using single-volcano or single hotspot averages. The data plotted in Figure 1 represent the authors' best effort to provide a representative sampling of OIB data. They include several oceanic plateaus, as well as several EM-type hotspots, which show slightly lower-than-average Nb/U ratios, consistent with the presence of some continent-derived material in their sources. Remarkably, the mean Nb/U ratio of all these OIBs, hotspots, volcanoes, and plateaus is Nb/U = 47.0 ±6.6 (1 std. dev.), which is indistinguishable from the MORB average of Nb/U = 46.1 ± 9.2 (Gale et al. 2013), as well as the value found by Hofmann et al. (1986) of 47 ±10. Our assessment of the similarity in Nb/U between MORB and OIBs is further substantiated by a plot of Nb/Th vs. Th (Fig. S1), which shows the same relationships but is not significantly affected by sample alteration.

In order to use a trace element ratio (instead of an isotope ratio) of basalts to characterize their source compositions, one needs to demonstrate that its value is independent of the degree of melting and therefore equal to the source ratio (Hofmann et al., 1986). Trace element ratios that meet this requirement are independent of absolute enrichment of the absolute concentrations of their incompatible elements, such as Th, are called "canonical." Figure 2 displays Nb/U, Nb/Th, Ta/U, and Nb/La as functions of the Th concentrations in the set of 583 MORB glasses analyzed by Jenner and O'Neill (2012a). This shows that, at least for MORB samples, Nb/U and Ta/U ratios do not significantly change, whereas Nb/Th decreases slightly as the Th concentration increases by a factor of about 100. By contrast, the Nb/La ratio increases systematically by roughly a factor of three over the same Th range. Thus, Nb/U and Ta/U appear to be suitable "canonical" ratios, and Nb/Th is nearly canonical, but Nb/La is not canonical.

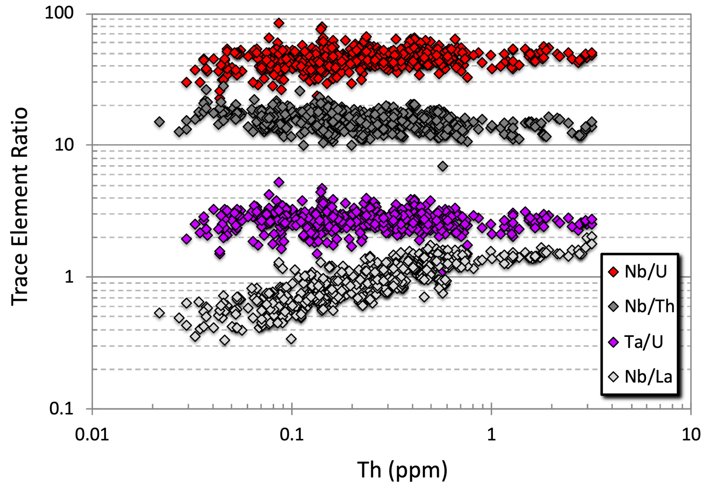


Fig. 2. Nb/U, Ta/U, Nb/Th, and Nb/La versus Th concentrations in about 600 MORB glasses. Data are from Jenner and O'Neill (2012a). This illustrates the essential requirements for selecting "canonical" trace element ratios: they must remain essentially constant and independent of source/melt depletion or enrichment in mantle-derived basalts. Nb/U and Ta/U meet this requirement nearly perfectly, whereas Nb/Th decreases slightly as a function of increasing Th. All three of these ratios are useful tracers of source composition. In contrast, Nb/La increases by about a factor of three as Th increases by two orders of magnitude. Thus, Nb/La is not a reliable tracer of source composition and should not be used as a "canonical ratio."

Sims and DePaolo (1997) pointed out that log (a) versus log (b) plots provide a statistically more rigorous assessment than the log (a)/(b) vs log (a) plot used by Hofmann et al. (1986). Figure S2 shows such logU-logNb and logU-logTa plots for three published datasets of global MORBs by Arevalo and McDonough, (2010), Jenner and O'Neill, (2012a), and Gale et al. (2013) to evaluate the slopes of these plots. Ideally, if these ratios were constant over the entire range of absolute concentrations, the slopes of such correlations would equal 1.0. The actual slopes for all three datasets are slightly lower than 1.0 for logU vs. logNb, and slightly greater than 1.0 for log U vs. logTa. Figure S3 shows how these slopes vary systematically for a larger range of trace element ratios, involving Ba, Th, U, Nb, Ta, K, and La. These systematic variations in slopes of log-log plots can be translated into a sequence of increasing compatibility of Ba < Th < Nb < U < Ta <K < La, based on global MORB data. We can also conclude from this analysis that both Nb/U and Ta/U closely approach the ideal "canonical" (i.e. invariant) status, but a ratio of uranium with an element with properties intermediate between Nb and Ta would be needed to form a perfectly invariant ratio.

Arevalo and McDonough (2010) raised the issue whether an element pair can be used for a "canonical" ratio that also characterizes its source, if its log-log slope deviates slightly from 1.0. To address this issue, we use a simple bracketing method. We calculate the size and composition of the source reservoir first for Nb/U, which consistently yields slopes slightly less than 1.0 in the log-log plots of Figure S2, and then for Ta/U, which consistently yields slopes slightly greater than 1.0. It turns out that the results are nearly indistinguishable, thus validating both ratios as being adequately "canonical" for the purpose at hand.

Table S3 shows the mean Nb/U, Ta/U, and Nb/Th ratios obtained from the three sets of MORB data. We note that the three data sets agree remarkably well. The most important exception is the value of Ta/U = 2.75 for average MORB by Jenner and O'Neill (2012a) which is significantly lower than the values of 2.91 and 3.09 given by Arevalo and McDonough (2010) and by Gale et al. (2013), respectively. This difference appears to be largely the result of an interlaboratory bias, because Jenner and O'Neill (2012b) report a Ta value for BCR-2G that is 6.7% lower than the preferred GeoReM value for this reference material (http://georem.mpch-mainz.gwdg.de). For the purpose of this paper, we will use values obtained by Gale et al. (2013).

2.2. Bulk-Silicate Earth Nb/U and Ta/U ratios

In this paper, we use Bulk Silicate Earth (BSE) values of Ta/U = 1.82 (McDonough and Sun, 1995) and Nb/U = 27.34, which is lower than McDonough and Sun's recommended value of 32.4. These values correspond to a BSE value of Nb/Ta = 15.5 instead of Nb/Ta = 17.78 (McDonough and Sun, 1995). This reduction of BSE niobium has a relatively minor effect on our quantitative results, but it is indicated by data; for example, nearly all known terrestrial silicate samples have lower-than-chondritic Nb/Ta, most likely due to incorporation of Nb in Earth's core (e.g Huang et al. 2020; see also Supporting Information).

3. Testing the 3-reservoir silicate Earth model by mass balance

3.1. Equations and input parameters 3 Data, or a descriptive heading about data

Following Davies (1981), the mass balance in a simple, three-reservoir silicate Earth consisting of the continental crust, the complementary depleted mantle reservoir, and a "left-over" primitive mantle reservoir, yields X_{dm}, the mass fraction of the depleted mantle reservoir

$$X_{dm} = \frac{X_{cc}\,\mathrm{C}_{cc}\,(\mathrm{R}_{dm} - \mathrm{R}_{cc})}{\mathrm{C}_{pm}\,(\mathrm{R}_{dm} - \mathrm{R}_{pm})} - X_{cc} \qquad (1)$$

where X is the mass fraction of a given reservoir, R is an isotopic or canonical chemical abundance ratio, C is the concentration of the chemical element in the denominator of R, and the subscripts *cc, pm*, and *dm* identify the three reservoirs continental crust, primitive mantle, and depleted mantle, respectively.

The concentration of the element in the denominator of ratio R is given by:

$$C_{dm} = \frac{\mathrm{C}_{pm}\,(X_{dm} + X_{cc}) - X_{cc}\,\mathrm{C}_{cc}}{\mathrm{X_{dm}}} \qquad (2)$$

For the readers' convenience, the derivation of equation (1) and (2) is given in the Supporting Information.

Here we initially specify *(Nb/U)* and *(Ta/U)* for *R*, in order to solve equations (1) and (2). Subsequently, we repeat this calculation using ε(Nd) for *R*, in order to compare the results. The input parameters for the primitive reservoir *pm* are taken from McDonough and Sun (1995), except for the value of Nb, which we reduce from 0.658 ppm to 0.555 ppm in order account for the Nb deficiency in the bulk silicate Earth (Section 2.3 and Supporting Information. The parameters for the continental crust U_{cc}, $(Nb/U)_{cc}$ and $(Ta/U)_{cc}$ are from Taylor and McLennan (1985), Rudnick and Fountain (1995), Rudnick & Gao, (2003), McLennan et al. (2006), and Hacker et al. (2015). These parameters are listed in Table S4. We note that the estimates for the crustal abundance of U in the above publications range from 0.91 to 1.4 ppm. Even higher values for the crustal U abundance can be found in the literature, but will not be considered here. We further note that the U value of = 0.91 ppm given by Taylor and McLennan (1985) was revised to U = 1.1 ppm by McLennan et al. (2006). A minimum of U = 1.1 ppm is also found in three of the five crustal models given by Hacker et al. (2015). The maximum value given by these authors is U = 1.33 ppm, and this is nearly identical to the value of U =1.3 ppm given by Rudnick and Gao (2003). We will use a range of crustal U = 1.1 to 1.3 ppm in the following calculations. Nb and Ta abundances of the bulk continental crust are less critical in the mass balance calculations. McLennan et al. (2006) and Rudnick and Gao (2003) give a value of Nb = 8 ppm, whereas the five models of Hacker et al. (2015) yield a range of Nb = 7.4 to 8.8 ppm. In contrast, the estimates of the above authors for Ta are more variable, ranging from Ta = 0.52 to 0.8 ppm. These variations in Nb and Ta estimates of the continental crust are the cause of the minor scatter in the mass balance results in Figure 3.

The initial assumption of a very simple, three-reservoir silicate Earth represents an important simplification. Indeed, such a model harks back to the time when Earth's mantle was widely thought to consist of a depleted upper and a primitive lower mantle, as discussed in the Introduction. In its simplest form, this model has largely been laid to rest by the findings of seismic tomography and geochemistry. We will use it as a starting point in our evaluation of the mantle reservoir involved in forming the continental crust. As already noted, it will be seen from our reevaluation of the analogous mass balance using Nd isotopes that this model is not adequate for describing Earth's silicate interior, and this result will lead us to postulate the existence of an additional, enriched, and now hidden or lost, reservoir.

3.2. Preliminary evaluation of the mass fraction of Depleted Mantle (DM) based on canonical ratios

Figure 3 shows the mass of the residual mantle, using equation (4) with our preferred input parameters $(Nb/U)_{BSE} = (Nb/U)_{pm} = 27.34$, $(Ta/U)_{bse} = (Ta/U)_{pm} = 1.82$, $(Nb/U)_{dm} = 46$, $(Ta/U)_{dm} = 3.09$, crustal Nb/U and Ta/U values given in Table S4, and showing a preferred range of crustal uranium contents between 1.1 and 1.3 ppm. Thus, "bracketing" the calculation with two nearly perfectly canonical ratios leads to virtually identical results, showing a mass fraction of DM ranging from $X_{dm} = 0.6$ to 0.8. In contrast, the gray dashed line based on a BSE with a strictly chondritic Nb/U ratio would require a DM mass fraction of $X_{dm} = 0.9$ to impossible values of $X_{dm} > 1.0$. Overall, Figure 3 demonstrates that, for the simple three-reservoir model, the mass of DM amounts to more than 60 percent of the total mantle, assuming a range of crustal U values of 1.1 to 1.3 ppm as discussed above, far exceeding the mass fraction of the upper mantle above 660 km (about 30% by mass) traditionally inferred in the literature on the basis of Nd isotopes.

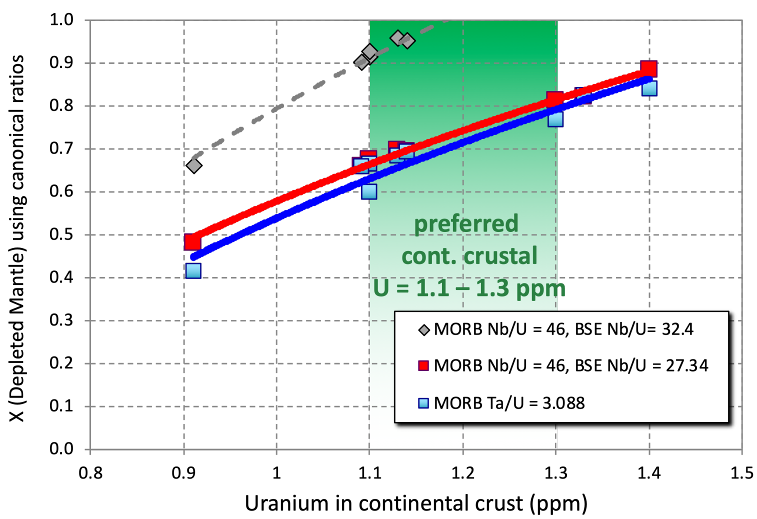


Fig. 3. Mass fraction of depleted mantle, X_{dm}, based on the canonical ratios Nb/U and Ta/U in a three-reservoir Earth model. X_{dm} is calculated from equ. (1) and a MORB average of Nb/U = 46 given by Gale et al. (2013) and Jenner and O'Neill (2012a), as well as Ta/U = 3.088 from Gale et al. (2013) as the R_{dm} parameters. The resulting value of X_{dm} depends significantly on the bulk U content assumed for the continental crust, U_{cc} . We use a variety of published crustal U estimates taken from Rudnick and Gao (2003), McLennan et al (2006), and Hacker et al. (2015), all within our "preferred range" of U_{cc} = 1.1 to 1.3 ppm, indicated by the green shaded region. The Nb/U and Ta/U-based results are in good agreement, if the reduced bulk silicate-Earth Nb value of 0.555 is used, yielding Nb/U 27.34 and Nb/Ta = 15.00 for the BSE (see text). By contrast, the dashed curve, using an uncorrected BSE abundance for Nb, displays significant disagreement with the Ta/U-based curve. The data points defining the red, blue and dashed lines correspond to crustal estimates of U and Nb in the literature (Hacker et al., 2015; McLennan et al., 2006; Rudnick & Fountain, 1995; Rudnick & Gao, 2003; Taylor & McLennan, 1985) listed in Table S4, where the different estimates mostly represent different assumptions about the lower crust composition.

3.3. Comparison with mass fraction of the Depleted Mantle (DM) based on Nd isotopes.

In order to compare the mass balances based on Nb/U or Ta/U with those based on Nd isotopes, we cannot simply use the Nd isotope data of the depleted MORB reservoir, as was done in the earlier estimates based on Nd isotopes, or even one based on all MORB data. This is because the (Nb,Ta)/U ratios shown in Figure 1 demonstrate clearly that the sources of both MORB and OIB must be included in this calculation. Thus, to validate such a comparison, we must attempt to include the Nd isotopic composition of the OIB source(s) as well, even though MORB and OIB show systematic isotopic differences. Figure 4a shows frequency plots for MORB data from Gale et al. (2013), which we regard as representing the isotopic composition of the global asthenosphere. Figure 4b shows the results of our compilation of average compositions for ocean islands and oceanic plateaus (Table S5). Taken together, these data should represent the entire mantle sampled by volcanism. Unfortunately, it is uncertain how these two families of mantle-derived basalts should be weighted to obtain a representative average for the entire mantle. Therefore, we once again use a bracketing approach by making two extreme assumptions: (1) the composition of DM is given by the MORB average of ε(Nd) = 8.6; (2) DM is represented by the averages of OIB ε(Nd) = 4.4 and oceanic plateaus of ε(Nd) = 5.8. We assume that the true value lies somewhere between these extremes.

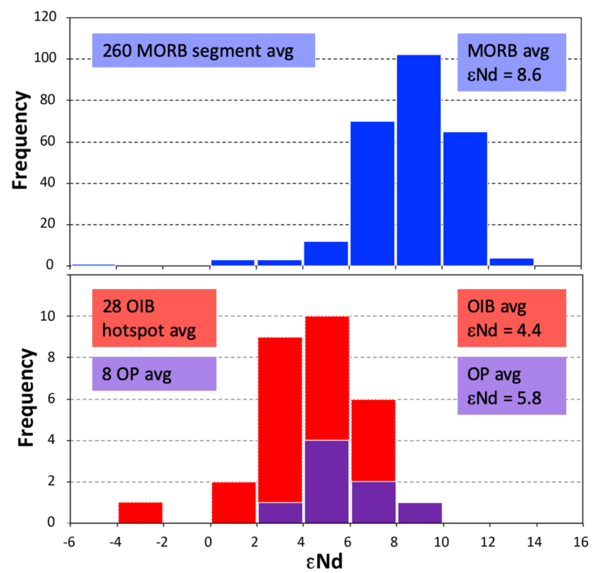


Fig. 4. Histogram of ε(Nd) values of mid-ocean ridge segment averages (Gale et al., 2013) and a new compilation of oceanic hotspot averages (Table S5). The OIB data for the 37 hotspots selected for this compilation are mostly those listed by Sleep (1990) and a few additional ones for which adequate ε(Nd) data exist. In addition, we compiled data for several oceanic plateaus. Each hotspot average represents the average value of individual volcano averages belonging to a given hotspot. The particular volcanoes selected are in some cases, such as Iceland, incomplete and somewhat arbitrary; they are largely governed by the availability of data. The hotspot data show a mean value of ε(Nd) = 4.4 ± 2.3 (1 std deviation), corresponding to a standard error of ±0.4 for 28 hotspots. The Pacific oceanic plateaus yield a mean value of ε(Nd) = 5.8. We also note that the hotspot averages have not been weighted for the plume flux given by Sleep (1990). We suggest that, given the existing sampling of hotspots, a perfectly representative distribution of hotspot isotopic compositions is probably not possible at the present time, but the data are adequate for our evaluation.

Figure 5 shows the results of the Nd-isotope-based mass balance calculations, using equation (1) for ε(Nd) values ranging from 8.6 (average MORB) down to ε(Nd) = 2 (a value even lower than average OIBs). For the continental crust, we choose a range of ε(Nd) = -10 to -17, which includes the estimates given by Goldstein et al. (1984), Goldstein and Jacobsen (1988), Rudnick (1990), and Chauvel et al. (2014). Figure 5 shows that the lowest possible mass fraction of the depleted mantle, X_{dm} = 0.2, is obtained by the combination of ε(Nd) = -10 for the continental crust and ε(Nd) = +8.6 for DM. The maximum value, obtained by the combination of ε(Nd) = -17 for the crust and +4.0 for the depleted mantle, respectively, is X_{dm} = 0.5. Thus, there is no overlap between this range (X_{dm} = 0.2 to 0.5) and the range obtained by the equivalent calculation based on Nb/U or Ta/U, namely X_{dm} = 0.6 to 0.8. We conclude that the inclusion of the OIB source reservoir is unable to reconcile the two independent mass balance calculations of a 3-reservoir silicate Earth, thus ruling out the simple 3-reservoir model for the Earth.

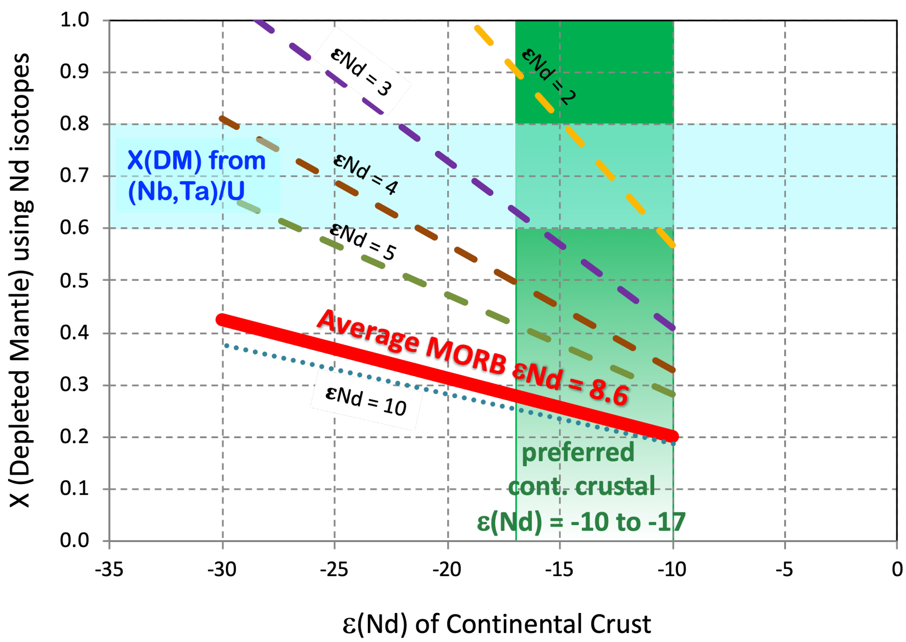


Fig. 5. Mass fraction of DM, X_{dm}, defined as the residue of continent extraction in a conventional three-reservoir Earth model (continental crust, depleted mantle, primitive mantle) based on Nd isotope ratios. Mass balance results are shown for a range of possible ε(Nd) values of mantle and average continental crust. The range of acceptable average continental values, ε(Nd) = -10 to -17 is taken from the literature (see text) and is indicated by the green shaded region. The ε(Nd) values assumed for DM range between the average MORB value (ε(Nd) = 8.6) to lower, less depleted values that might represent an integrated DM reservoir incorporating MORB+OIB sources, ε(Nd) = 5, 4, 3, 2. If DM occupies a mass fraction of = 0.6 to 0.8 (blue shaded region, taken from the Nb/U-based mass balance shown in Fig. 3), the ε(Nd) value of such

an integrated MORB+OIB reservoir would have to be unrealistically low (ε(Nd) ≤ 3.5). This is inconsistent with observed ε(Nd) values of average MORB (8.6), average OIB (4.4), and oceanic plateaus (5.8); see also Fig. 6

We further examine this result by calculating the composition of DM from equation (2) using its mass fraction and the estimated composition of the continental crust by Rudnick and Gao (2003) – RG, and McLennan et al. (2006) – MTH (Fig. 6). A DM mass fraction as small as X_{dm} = 0.3 results in several of the most highly incompatible elements in DM to have negative concentrations, which is of course physically impossible, providing independent confirmation that the present-day continental crust was extracted from much more of the mantle than just its upper part.

Another awkward feature of the conventional small volume, highly depleted DM is examined in Figure S4, which is an iteration of the partial melting model of Workman and Hart (2005), who calculated a melt fraction of 6% to generate an average MORB composition from their depleted mantle. By simply replacing the so-called "N-MORB" average used by Workman and Hart (2005) by the modern, more representative ALLMORB average given by Gale et al. (2013), Figure S4 shows that a melt fraction of 3% would be required to generate ALLMORB from such a Workman-Hart-type DM reservoir. Such a low melt fraction is at odds with independent estimates of MORB melting, which range from 8 to 20% melt fractions (Klein & Langmuir, 1987). Finally, our results reinforce Campbell's (2002) conclusion, based on partial melting modeling, that extraction of the continental crust contributes only a portion of the observed change in Sm/Nd and consequently ε(Nd) of the residual mantle.

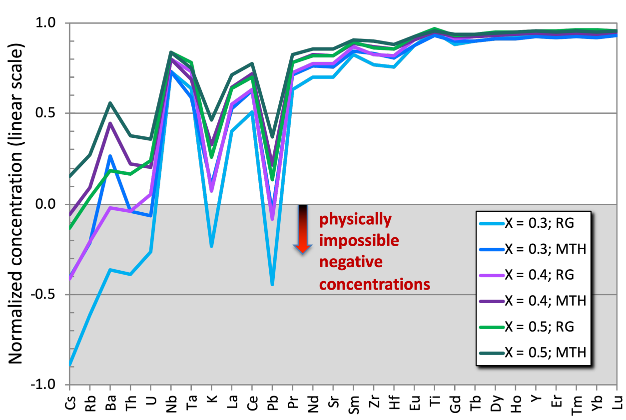


Fig. 6. Three-reservoir mass balance based on MORB ε(Nd) yields impossible results: DM compositions (PM-normalized) calculated from the mass balance equation (2), for conventional, ε(Nd)-based mantle models that limit the mass fraction X_{dm} of the depleted mantle to less than 50% of the total mantle. The case of X_{dm} = 0.3 corresponds to a DM reservoir restricted to the upper 660 km of the mantle. Results are shown for X_{dm} = 0.3, 0.4, and 0.5, and for continental crustal compositions given by Rudnick and Gao

(2003) – RG, and McLennan et al. (2006) - MTH. Especially for the case of $X_{dm} = 0.3$, several of the most highly incompatible elements, including Th and U, end up with (physically impossible) negative concentrations in the DM for both bulk crustal compositions. This provides additional, independent evidence that conventional, ε(Nd)-derived continental crust-mantle mass balances are based on incorrect assumptions.

3.4. What causes the discrepancy between the two depleted mantle (DM) estimates?

Our mass balance based on ε(Nd) explicitly included the OIB source reservoir(s), in addition to the traditionally used MORB source reservoir, to represent the DM complement of the continental crust. In spite of its inclusion in the mass balance, the OIB source reservoir(s) are not sufficiently enriched to yield a mass balance that is consistent with the (Nb,Ta)/U-based mass balance. This means that there must be at least one additional enriched (i.e. low-ε(Nd)) reservoir to achieve an overall mass balance for the bulk silicate Earth, assuming that BSE possesses chondritic ε(Nd), Ta/U, and near-chondritic Nb/U values. Such an additional enriched reservoir may have been lost from the Earth by collisional erosion, as suggested e.g. by O'Neill and Palme (2008). Alternatively it may be hidden in the lowermost mantle in form of an EER (= early enriched reservoir), as proposed by Tolstikhin and Hofmann (2005) and Boyet and Carlson (2005). Below, we will further explore the option of an early-enriched reservoir. This will force us to expand the 3-reservoir BSE to a 4-reservoir BSE.

4. The four-reservoir silicate Earth

4.1 The hidden, early-enriched reservoir (EER) and the early-depleted reservoir (EDR)

We suggest that an early-enriched reservoir (EER) is generated by the formation and permanent sequestration of an early mafic crust. This EER is similar but not identical to the EER suggested by Boyet and Carlson (2005, 2006) on completely different grounds, namely their discovery of elevated, non-chondritic $^{142}Nd/^{144}Nd$ ratios of the (accessible) bulk silicate Earth (as represented by continental crust, MORB, and OIB). The composition of Boyet and Carlson's EDR (Early Depleted Reservoir) and its complementary EER were estimated in part by a mass balance involving a Depleted Mantle reservoir derived from a crust-mantle differentiation model similar to that developed by Workman and Hart (2005). This model, in turn, involved the composition of the present-day continental crust (which did not exist at the time of EER sequestration), and this imparted a substantial negative Nb anomaly on the trace element pattern of the EDR of Boyet and Carlson (2005, 2006). We suggest that this anomaly is a result of adding the present-day continental crust to the modeled present-day MORB source, an approach that must now be abandoned because we have shown that the present-day MORB source cannot be the simple complement of the present-day continental crust (more details are in Supporting Information B).

Here we model EER using a simple batch melting process that generates a now-lost early mafic crust. We sequester (by subduction or loss to space) a small amount it, leaving behind a large, moderately depleted EDR, which occupies the remainder of the mantle. The EDR then differentiates into the continental crust and the depleted mantle (MORB + OIB) reservoir, which we call "Residual Mantle" (RM) for the 4-reservoir model to distinguish it from the 3-reservoir model, in which the residue of the continental crust was referred to as "Depleted Mantle" (DM). Because of the permanent sequestration of the EER, we can reformulate equation (1) for the subsequent differentiation of EDR into CC (continental crust), Residual Mantle (RM), incorporating both MORB and OIB sources, and a "left-over" amount of EDR. This reformulation amounts to a modified 3-reservoir system (plus an isolated EER) and the reformulated equation (1) will be labeled equations (3) and (4) as discussed below:

The two new balance equations, one formulated for (Nb/U), the other for ε(Nd), can be solved to find a common (identical) value of the mass fraction of the residual mantle.

$$X_{RM} = \frac{X_{CC}\, Nd_{CC}\,(\varepsilon_{RM} - \varepsilon_{CC})}{Nd_{EDR}\,(\varepsilon_{RM} - \varepsilon_{EDR})} - X_{CC} \qquad (3)$$

$$X_{RM} = \frac{X_{CC}\, U_{CC}\,(Nb/U_{RM} - Nb/U_{CC})}{U_{EDR}\,(Nb/U_{RM} - Nb/U_{EDR})} - X_{CC} \qquad (4)$$

If the EER is permanently lost from Earth by collisional erosion (O'Neill and Palme, 2008), the mass fractions calculated from equations (3) and (4) will equal the actual mass fractions in the silicate Earth. If, on the other hand, EER remains buried in the mantle, these mass fractions will have to be reduced by a factor of $(1 - X_{eer})$ in order to correspond to the actual mass fractions of the total silicate Earth. There are four unknowns, X_{rm}, Nd_{edr}, ε_{edr} , U_{edr}, in equations (3) and (4), with ε short for *ε(Nd)*. However, using a simple model of partial melt segregation for generating the EDR, we can replace three of these variables by a single one, X_{eer}. This is because for a given melt fraction F and age of the silicate Earth, say F = 0.1 and 4.57 Ga, the melt segregation model uniquely determines Nd_{edr}, ε_{edr} , and U_{edr}, as a function of the sequestered melt fraction, namely the Early Enriched Reservoir, X_{eer}. In this approach ε_{edr} is calculated from the resulting Sm_{edr} combined with Nd_{edr} , and using the radioactive decay equation to determine the present-day $^{147}Sm/^{144}Nd$ ratio. We thus have only two variables, X_{EER} and X_{RM} to solve the two equations (3) and (4), as for each value of X_{EER} there is a specific value of Nd_{EDR}, U_{EDR} and ε_{EDR} , which is determined by the equations for partial melting and radioactive decay, respectively. The solution is then given by the intersections of the two functions (3) and (4), as shown in Fig. S5.

We solved this system of equations numerically, using partitioning data for spinel lherzolite given by Salters and Stracke (2004). Specific values of these solutions for X_{rm} , ε_{edr} , X_{eer} are given in Table S6. Figure 7 shows the results for an assumed melt fraction of F = 0.1 to generate the now-lost early mafic crust. Figure 7a gives the range of mass fractions of RM as a function of its ε_{rm} value, covering the range of ε_{rm} = 4.5 to 8.5, that is, the possible mixtures of OIB and MORB averages discussed earlier. In order to explore the full range of solutions, we plot the results for the four possible combinations of the extreme values of the crustal composition estimates, U_{CC} = 1.1 and 1.3 ppm, ε_{CC} = -10 and -17. The central red line shows the results for intermediate values, namely ε_{CC} = -12 and U_{CC} = 1.2 ppm for the continental crust. The important result is that the possible mass fractions of residual mantle range from about 72% to nearly 100% of the mantle (except for the 1 to 3% occupied by the EER). Figure 7b shows the corresponding mass fractions of the sequestered EER, which range from about 1-3% of the mantle. Figure

7c shows the respective ε_{EDR} values. In both cases, using a crustal U value of 1.3 ppm (Rudnick & Gao, 2003), the range of ε_{EDR} and X_{EER} is "cut off" by the fact that *X(RM)* has reached or exceeded 98% of the mantle (Fig. 7a), so that the EDR has been completely used up to make CC and RM.

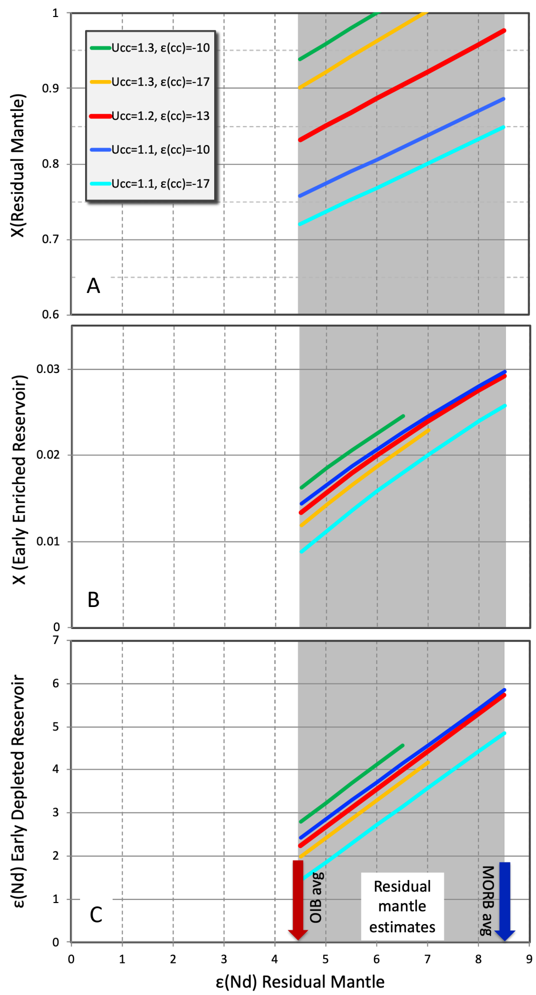


Fig. 7

Fig. 7. Specific solutions for the new 4-reservoir models described by equations (3) and (4), all plotted against the full range of $\varepsilon(Nd)_{rm}$ values ($\varepsilon(Nd) = 4.5$ to 8.5) of the combined MORB-plus-OIB source reservoir. Models are calculated for an EER formed by a (batch) melt fraction of $F = 0.10$, using partition coefficients for spinel lherzolite from Salters and Stracke (2004). (7a) Mass fraction of residual mantle, Xrm versus ε(Nd)rm for crustal compositions with Ucc = 1.1 and 1.3 ppm, and ε(Nd)cc = -10 and -17, representing the extreme range of assumed crustal compositions. (7b) Mass fraction of the Early Enriched Reservoir, Xeer, for the same range of crustal compositions. (7c) ε(Nd)edr for the same range of crustal compositions.

Figure 8 shows the effect of varying the melt fraction that generates the now-lost early mafic crust and thus the EER, using alternative melt fractions of F = 0.08 and 0.12. For clarity, we restrict this to the case of an intermediate crustal composition of U_{cc} = 1.2 ppm and ε_{Nd} = -12. We infer from these results that the scope for varying the melt fraction generating EER is limited. Higher melt fractions are limited by the fact that X_{rm} cannot exceed (BSE-X_{eer}), about 0.98. Smaller melt fractions cause the size of *X(RM)* to be only slightly lower, but would require the generation of more and more alkaline melts, such as are not found, for example, in Archean greenstones. All solutions yield X_{RM} > 70% of the total mantle, and in the more U-rich crustal models, especially the crustal U estimate of Rudnick and Gao (2003), the residual reservoir may occupy more than 90% of the mantle. Nevertheless, most models leave room for a significant amount of EDR in the mantle.

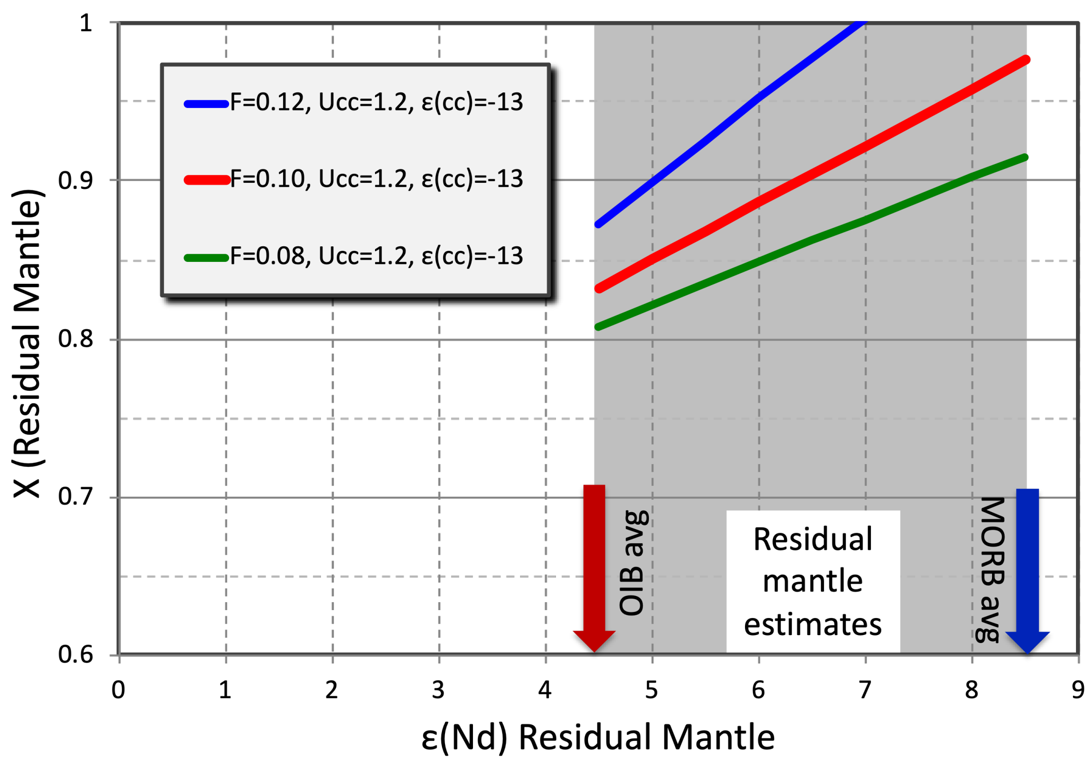
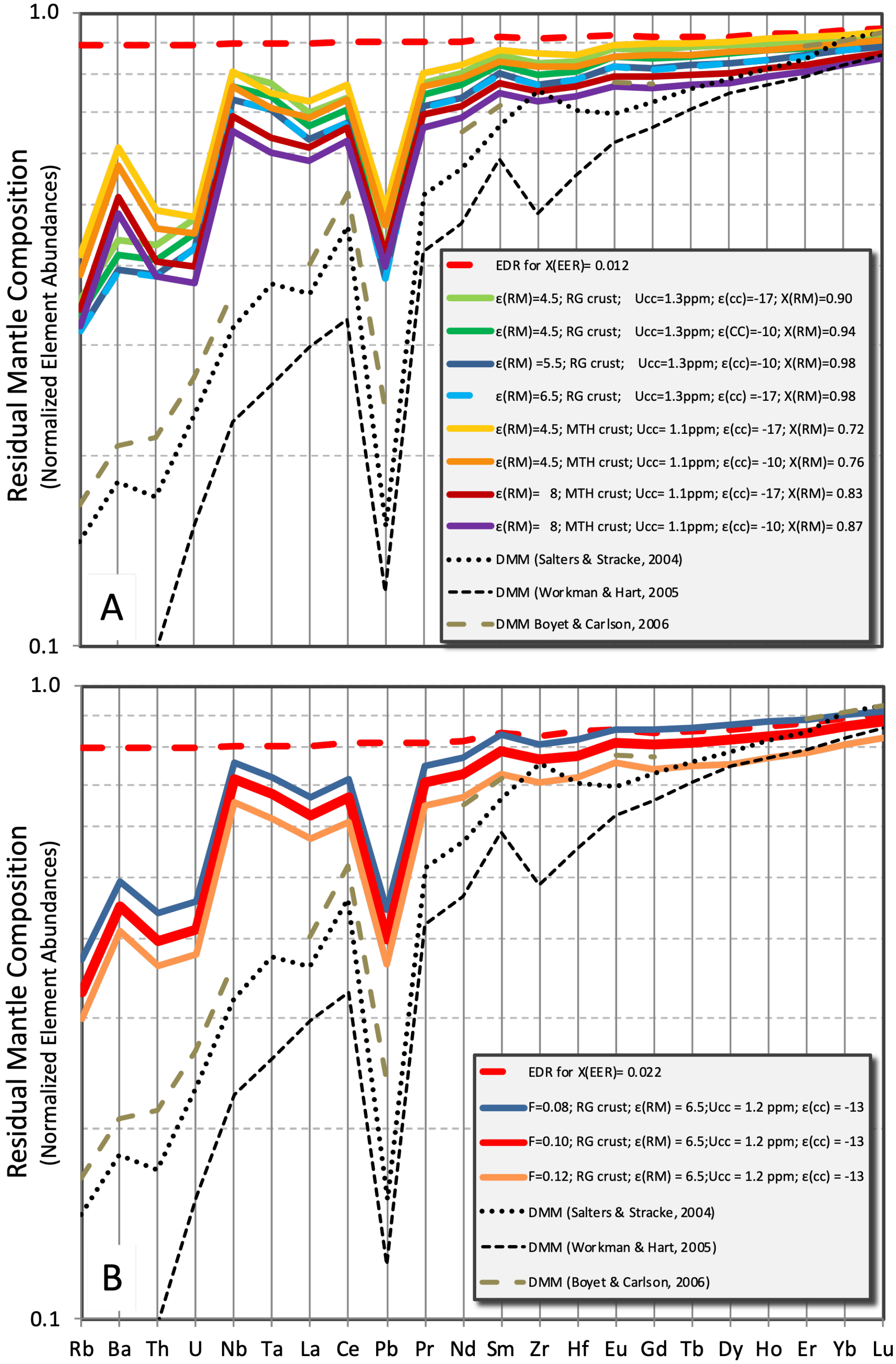


Fig. 8. Solutions of equations (3) and (4) for three different melt fractions forming EER, F= 0.08, 0.10, and 0.12. The crustal composition assumed here is an intermediate value of the one used in Figure 7, namely U_{cc} = 1.2 ppm, and $\varepsilon(Nd)_{cc}$ = -13.

With the above results, in particular the values for *X(RM)* given in Figure 7a, we can now calculate the trace element abundances of RM, using a modified version of equation (2), in which the Primitive Mantle is replaced by the EDR:

$$C_{RM} = \frac{\mathrm{C}_{EDR}\,(X_{RM} + X_{CC}) - X_{CC}\,\mathrm{C}_{CC}}{\mathrm{X}_{RM}} \tag{5}$$

Figure 9 shows the element abundances of the residual mantle for the same range of crustal compositions used further above, and for a range of choices for the *ε(Nd)* composition of the residual mantle. In order to cover the full range of solutions, Fig. 9a gives the Residual Mantle abundances for an Early Enriched Reservoir generated by a melt fraction of F = 0.10 and the extreme values of the continental crust, ε(Nd) = -10 and -17, and uranium concentrations of U = 1.1 and 1.3 ppm and extreme values of ε(Nd) of the Residual Mantle of 4.5 and 8.0. In cases where the calculated total mass fraction of the Residual Mantle exceeds X_{rm}=0.98, an appropriately lower value of ε(RM) is used. Figure 9b illustrates the effect of varying the initial melt fraction of EER. We suggest that the melt fraction cannot be arbitrarily increased to even higher values, because this would require the sequestration of seemingly unreasonably large EERs. At F = 0.12, the size of the EER would already be quite large, X(EER) = 2.5 to over 4%.



Residual Mantle Composition
(Normalized Element Abundances)
1.0
0.1
A
EDR for X(EER)= 0.012
ε(RM)=4.5; RG crust; Ucc=1.3ppm; ε(cc)=-17; X(RM)=0.90
ε(RM)=4.5; RG crust; Ucc=1.3ppm; ε(CC)=-10; X(RM)=0.94
ε(RM) =5.5; RG crust; Ucc=1.3ppm; ε(cc)=-10; X(RM)=0.98
ε(RM)=6.5; RG crust; Ucc=1.3ppm; ε(cc) =-17; X(RM)=0.98
ε(RM)=4.5; MTH crust; Ucc= 1.1ppm; ε(cc)= -17; X(RM)= 0.72
ε(RM)=4.5; MTH crust; Ucc= 1.1ppm; ε(cc)= -10; X(RM)= 0.76
ε(RM)= 8; MTH crust; Ucc= 1.1ppm; ε(cc)= -17; X(RM)= 0.83
ε(RM)= 8; MTH crust; Ucc= 1.1ppm; ε(cc)= -10; X(RM)= 0.87
DMM (Salters & Stracke, 2004)
DMM (Workman & Hart, 2005
DMM Boyet & Carlson, 2006
B
EDR for X(EER)= 0.022
F=0.08; RG crust; ε(RM) = 6.5;Ucc = 1.2 ppm; ε(cc) = -13
F=0.10; RG crust; ε(RM) = 6.5;Ucc = 1.2 ppm; ε(cc) = -13
F=0.12; RG crust; ε(RM) = 6.5;Ucc = 1.2 ppm; ε(cc) = -13
DMM (Salters & Stracke, 2004)
DMM (Workman & Hart, 2005)
DMM (Boyet & Carlson, 2006)
Rb Ba Th U Nb Ta La Ce Pb Pr Nd Sm Zr Hf Eu Gd Tb Dy Ho Er Yb Lu

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Fig. 9a. Normalized incompatible-element plots for the models shown in Figure 7. Shown are the Residual Mantle compositions corresponding to two crustal compositions of Rudnick and Gao (2003) and McLennan et al. (2006), labeled RG crust and MTH crust, respectively. Normalizing concentrations are from McDonough and Sun (1995).

Fig. 9b. Normalized incompatible-element plots for the models shown in Figure 8. Shown are the Residual Mantle compositions corresponding to the averages of the two crustal concentration values of Rudnick and Gao (2003) and McLennan et al. (2006). The 3 solid lines correspond to F = 0.08, 0.10, and 0.12 as in Fig. 8. Also shown is the corresponding composition of Early Depleted Reservoir, EDR, for the case of F= 0.1. For comparison, we also show the abundance patterns of the traditional Depleted Mantle (DMM) models of Salters and Stracke (2004). Workman and Hart (2005) and Boyet and Carlson (2006).

The resulting Th and U abundances of the residual mantle are all significantly higher than the three published DMM estimates, even though the corresponding X_{RM} values range from about 70% to nearly 100% of the total mantle. The seemingly strange positive Ba anomalies in the RM trace element patterns using the crustal abundances of McLennan et al. (2006), is the result, possibly an artifact, of their relatively low Ba abundances (250ppm versus 540 ppm for the Rudnick-Gao crust) of their crustal model.

For comparison, we also show the abundance patterns of the traditional Depleted Mantle (DMM) models of Salters and Stracke (2004). Workman and Hart (2005) and Boyet and Carlson (2006). Thus, the actual Residual Mantle that is chemically complementary to the continental crust is far less severely depleted in highly incompatible elements than had been inferred by previous evaluations of the DM composition. In particular, the heat production (as given by the Th and U abundances) of the Residual Mantle is now seen to be two to five times higher than previously thought.

In order to assess the question of how sensitive our results are to the precise value of the Nb/U and Ta/U ratios of the Residual Mantle, we compare results for Nb/U = 42, 46, and 50 for a Residual Mantle generated by crustal values of Ucc = 1.2 ppm and ε(cc) = -13 (Fig. 10). Thus, if the Nb/U ratio of the Residual Mantle were as high as 50, its mass fraction would be substantially reduced, especially at the lowest value of ε(RM) = 4.5, but it would still exceed 70% of the total mantle.

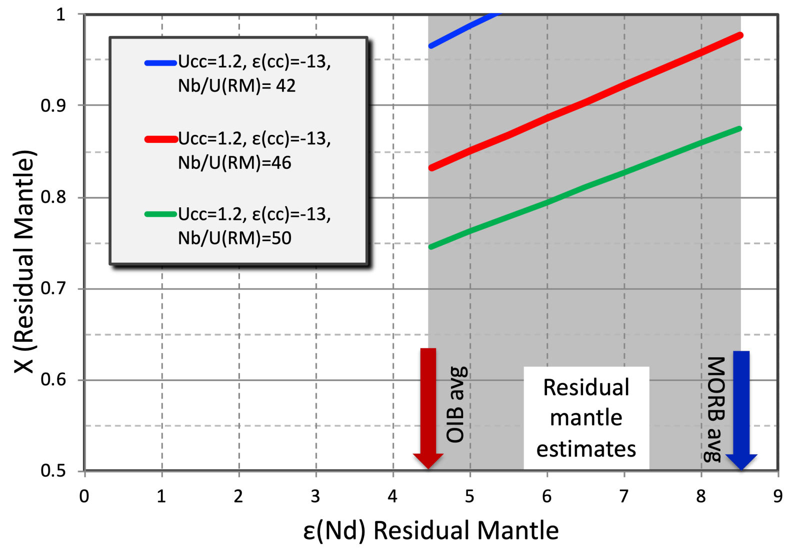


Fig. 10. Same as Fig. 8, but assuming three values of Nb/U for the Residual Mantle, Nb/U = 42, 46, and 50. This explores how sensitive the results are to the precise value of $(Nb/U)_{rm}$ used for the mass balance calculation. Even though this range is much larger than the standard errors of both the MORB and the OIB data, this shows that the minimum mass fraction of the Residual Mantle, Xrm, is still greater than 70%.

The preceding discussion has shown that, depending on the specific assumptions about the isotopic and elemental composition of the crust and the present-day mantle, a fairly wide range of solutions is possible for size and composition of Earth's residual mantle. What all of these solutions have in common though is that the mantle residue of the present-day continental crust fills at least 70%, and possibly nearly all of the mantle, and it is substantially less depleted in incompatible elements than previously thought. Table 1 gives the calculated composition for a residual mantle and continental crust that is compositionally intermediate between the more extreme values used in the preceding calculations. This gives the normalized "average" composition for a combined MORB-plus-OIB source mantle characterized by ε(Nd) = 6.5, a melt fraction generating the Early Enriched Reservoir of F= 0.10, and a crustal composition that is an average between the values given by Rudnick and Gao (2003) and by McLennan et al. (2006). Its uranium and thorium abundances are close to 40% of their respective primitive mantle values.

Table 1. Composition of the residual mantle

(1) Creation of an early-depleted reservoir (EDR) by extracting an early-enriched basaltic reservoir (EER).
The EER is generated from primitive mantle by batch melting (F = 10 %) and sequestering a mantle mass fraction of X(EER) = 0.022 of this melt

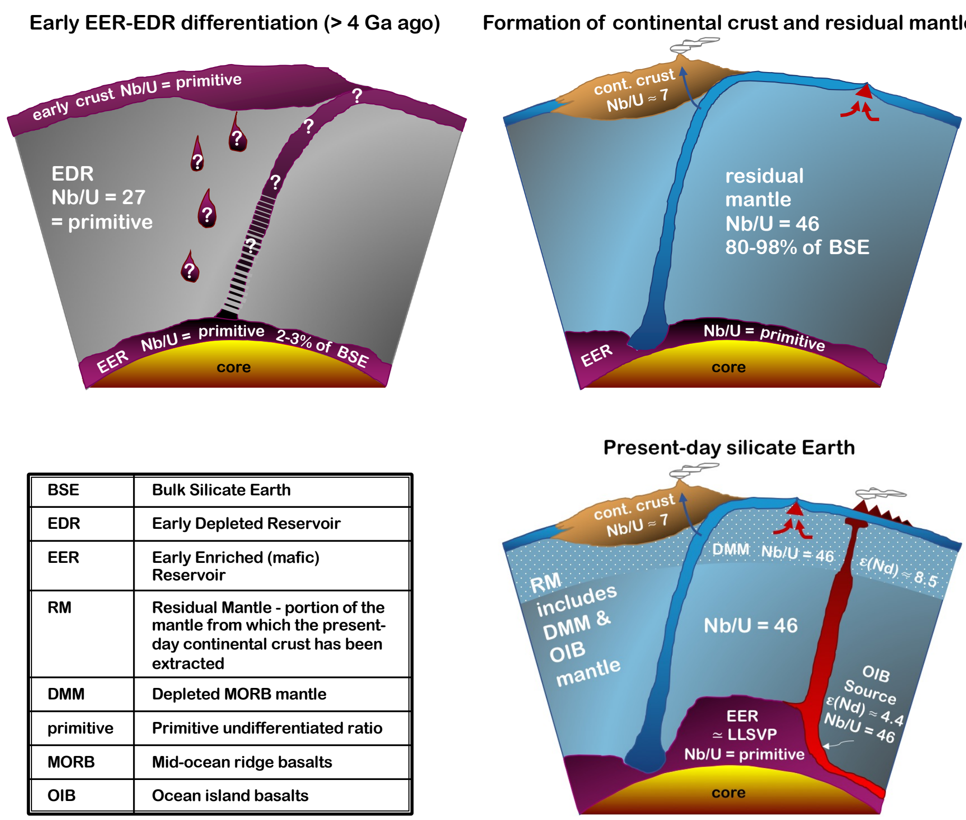
(2) Differentiation of EDR into continental crust and Residual Mantle (RM)
This Table also shows published estimates of Depleted Mantle (DM) compositions for comparison

				Cont. Crust normalized	**Cont. Crust normalized**	**Cont. Crust normalized**	Residual Mantle, this paper X(rm)= 0.905, ε(rm) = 6.5	Depleted Mantle, Literature SS[3]	Depleted Mantle, Literature WH[3]	Depleted Mantle, Literature BC[3]
	Primitive Mantle	F(eer) = 0.1 X(eer) = 0.022	After EER extraction	RG[2]	MTH[2]	Average (RG+MTH)	Average crust (RG & MTH)	Depleted Mantle (DMM)norm.	Depleted Mantle (DMM)norm.	Depleted Mantle (DMM)norm.
		C(eer)norm	**C(edr)norm**	**C(cc)norm**	**C(cc)norm**	**C(cc)norm**	**C(rm)norm**	**C(dmm)norm**	**C(dmm)norm**	**C(dmm)norm**
Rb	0.6	9.98	0.798	81.67	81.67	81.67	**0.328**	0.147	0.083	0.167
Ba	6.6	10.00	0.797	69.09	37.88	53.48	**0.448**	0.182	0.085	0.208
Th	0.0795	9.89	0.800	70.44	52.83	61.64	**0.396**	0.172	0.099	0.201
U	0.0203	9.85	0.801	64.04	54.19	59.11	**0.414**	0.232	0.156	0.266
Nb[1]	0.555	9.74	0.803	14.41	14.41	14.41	**0.713**	0.319	0.226	0.432
Ta	0.037	9.74	0.803	18.92	21.62	20.27	**0.674**	0.373	0.259	
La	0.648	9.68	0.805	30.86	24.69	27.78	**0.626**	0.361	0.296	0.401
Ce	1.675	9.35	0.812	25.67	19.70	22.69	**0.667**	0.461	0.329	0.519
Pb	0.15	9.27	0.814	73.33	53.33	63.33	**0.399**	0.155	0.122	0.233
Pr	0.254	9.27	0.814	19.29	15.35	17.32	**0.704**	0.516	0.420	
Nd	1.25	9.07	0.818	16.00	12.80	14.40	**0.728**	0.570	0.465	0.645
Sm	0.406	7.84	0.846	9.61	8.62	9.11	**0.791**	0.665	0.588	0.722
Zr	10.5	8.46	0.832	12.57	9.52	11.05	**0.764**	0.756	0.484	
Hf	0.283	7.67	0.850	13.07	10.60	11.84	**0.777**	0.703	0.555	0.767
Eu	0.154	7.49	0.854	7.14	7.14	7.14	**0.812**	0.695	0.624	0.747
Gd	0.544	7.91	0.844	6.80	6.07	6.43	**0.807**	0.726	0.658	0.776
Tb	0.099	7.72	0.849	6.06	6.06	6.06	**0.814**	0.758	0.704	
Dy	0.674	7.57	0.852	5.34	5.49	5.42	**0.822**	0.788	0.749	
Ho	0.149	7.05	0.864	5.17	5.23	5.20	**0.835**	0.819	0.772	
Er	0.438	6.66	0.872	4.79	5.02	4.91	**0.846**	0.847	0.795	0.881
Yb	0.441	5.97	0.888	4.31	4.99	4.65	**0.863**	0.909	0.827	0.909
Lu	0.0675	5.40	0.901	4.44	4.44	4.44	**0.877**	0.933	0.859	0.933

1) The primitive mantle value of Nb = 0.658 given by McDonough and Sun (1995) has been adjusted to Nb = 0.555 ppm (see text).
2) Crustal compositions: RG = Rudnick and Gao (2003); MTH = McLennan et al., (2006)
3) Previously published Depleted Mantle values: SS = Salters and Stracke (2004); WH = Workman and Hart (2005; BC = Boyet and Carlson (2006)
Partition coefficients are for spinel lherzolite (Salters and Stracke, 2004)

5. Is the Early Enriched Reservoir hiding in the LLSVPs?

Finally, we briefly discuss the possibility that the Early Enriched Reservoir may be located near the core-mantle boundary, within the LLSVPs (Large Low Shearwave Velocity Provinces), as shown in our cartoon of mantle evolution (Figure 12). The LLSVPs have been recognized and delineated by seismologists relatively recently (e.g. Dziewonski et al., 2010; Garnero & McNamara, 2008). Their estimated mass ranges from 2% (Burke et al., 2008) to 9% of the silicate Earth (Cottaar & Lekic, 2016). Their ages have been traced by geological evidence from hotspots and kimberlite for at least 300 Ma (Burke et al. 2008), but their actual age is essentially unknown; thus it might well approach the age of the Earth. Most workers agree that the LLSVPs are compositionally different from the surrounding and overlying mantle rocks. It is therefore possible that an early-enriched reservoir, as well as an essentially primitive reservoir, have survived in these LLSVPs (e.g. Lau et al., 2017). For example, Ballmer et al. (2016) propose a geodynamic model whereby the lower portion of the LLSVP is primitive, and the upper portion consists of recycled basaltic crust. Although our simplified four-reservoir treatment does not specifically address these issues, it is consistent with the existence of LLSVPs possessing a relatively complex internal structure and compositional contrasts. Recent noble gas analyses of Xe, Ne and He in Iceland basalts compared with MORB also demand the formation and survival of an EER to explain the observed isotopic distinctions (e.g. Mukhopadhyay, 2012). We suggest that the noble gases contained in the EER leak into the mantle-plume sources by diffusion. This is consistent with dynamic Earth models in which plumes are derived predominantly from the boundary layer above the LLSVPs, because the refractory elements in mantle plumes are dominated by recycled oceanic lithosphere that is significantly younger than the EER and possesses elevated (Nb,Ta)/U ratios caused by the extraction of continental crust.



BSE	Bulk Silicate Earth
EDR	Early Depleted Reservoir
EER	Early Enriched (mafic) Reservoir
RM	Residual Mantle - portion of the mantle from which the present-day continental crust has been extracted
DMM	Depleted MORB mantle
primitive	Primitive undifferentiated ratio
MORB	Mid-ocean ridge basalts
OIB	Ocean island basalts

Fig. 11

Fig.11. Cartoon of a possible crust-mantle evolution consistent with the constraints imposed by the combined evaluation of ε(Nd) and (Nb,Ta)/U-based mass balances. (a) Initial differentiation of the primitive mantle into an EER (Early-Enriched Reservoir) by forming and subducting a mafic early (possibly primordial) crust, leaving behind a slightly depleted Early Depleted mantle (EDR) with primitive (Nb,Ta)/U but fractionated Sm/Nd. (b) Subsequent differentiation of the EDR into continental crust having Nb/U = 7 and a Residual Mantle Reservoir (RM) having Nb/U = 46. In this particular version, the RM occupies all of the mantle except the EER, but the uncertainties of the model allow up to about 30% EDR surviving in the mantle. Present day mantle: the residual mantle has undergone additional differentiation into MORB and OIB sources, and the EER has accumulated in the two LLSVPs in the lowermost mantle.

6. Summary

We have reevaluated the global crust-mantle differentiation of the classical three-reservoir (primitive mantle, depleted MORB-mantle, continental crust) silicate Earth. We have found that no version of this model is able to simultaneously account for the observed (Nb,Ta)/U and the ε(Nd)-relationships used as measures of crust-mantle differentiation.

The conflicting mass balance constraints can be reconciled with a four-reservoir Earth model (Fig. 11) including an additional, early-enriched mantle reservoir (EER), now hidden within the Earth or lost to space, and its complement, the early-depleted reservoir (EDR – Fig.11a). We assume that these reservoirs formed early in Earth history, and Nb/U and Ta/U ratios in the EER and EDR are not fractionated relative to the primitive mantle (27.34 and 1.82, respectively). The EDR serves as the source for the continental crust (Fig. 11b). Nb/U and Ta/U ratios are fractionated during continent formation. The residue of continental crust formation over geologic time from the EDR is the Residual Mantle, which occupies at least 70% of the total mantle, and it may occupy all of it, except for the EER itself. This means that less than 30%, and quite possibly none, of the original EDR survives to the present day. To our knowledge, there are currently no hotspots that could be directly traced to an EDR source characterized by their primitive Nb/U $\simeq$ 30, it seems plausible that all of the original EDR has been differentiated into continental crust and present-day Residual Mantle.

The EER and possible remnants of the EDR may reside in the present-day LLSVP. They are likely to have originated by the differentiation of an early mafic crust characterized by a lower-than-primitive Sm/Nd ratio but primitive (Nb,Ta)/U ratios. The EER is conceptually similar to that postulated by Tolstikhin and Hofmann (2005) on the basis of xenon isotopes and by Boyet and Carlson (2005) on the basis of ^{142}Nd isotopes, but its composition differs significantly from the specific EERs postulated by Boyet and Carlson (2005) and Carlson and Boyet (2008) and from the collisionally eroded crust of O'Neill and Palme (2008) and of Jackson and Jellinek (2013). Alternatively, our results are consistent with models of deep burial of the EER or with its removal from the Earth by collisional erosion.

In conclusion, classical ε(Nd)-based estimates of the size and composition of the depleted mantle are systematically in error. We have shown that no simple 3-reservoir mantle model consisting of a chondrite-derived, primitive reservoir, a continental crust, and a depleted mantle reservoir is simultaneously consistent with the mass-balance constraints imposed by the observed Nd isotopic compositions and the (Nb,Ta/U) ratios of mantle and crust. This discrepancy exists whether the Nd isotopic mass balance takes into account only MORB or both MORB+OIB.

The Residual Mantle is much less depleted in highly incompatible elements, in particular the heat producers Th and U, than given by the classical Nd isotope-based estimates. Thus, the heat production of the present-day Residual Mantle, comprising both MORB and OIB sources, is about 40-50% of the bulk silicate value, rather than 10–20% as estimated by traditional, isotope-based models. The distribution of these heat sources between the relatively more enriched OIB sources and the more depleted MORB sources should be a subject of future investigations.

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Open Research

There are no original data presented in this paper. All geochemical data presented are from the literature and are referenced.

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