Size and composition of the residual and depleted mantle reservoir

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Key Points

(1) Conventional assessments of the size of the depleted mantle (30%), based on Nd isotopes, conflict with a new assessment based on Nb/U and Ta/U (> 60%).

(2) This conflict cannot be reconciled within the framework of the classical 3-reservoir silicate earth (continental crust, depleted mantle, primitive mantle).

(3) These results require segregation of a fourth, early-enriched, small reservoir. The continental crust is then extracted from almost all (80 to 98%) of the mantle.

Key words:
1009 Geochemical Modeling
1025 Composition of the Mantle
1038 Mantle process
1040 Radiogenic isotope geochemistry
1065 Major and trace element geochemistry

Plain Language Summary

The Earth's continental crust makes up only about one half of a percent of Earth's mass, but it contains a large portion of its total budget of many chemical elements such as potassium and phosphorus, which are critical to soil fertility, or 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 the mantle, the 3000 km thick layer of rocks beneath the crust. Therefore, part of the mantle is now depleted in these important chemical elements. But what portion of the mantle was involved in making the continents? In the past, geochemists thought that only its uppermost third was involved, leaving the lower two-thirds of the mantle essentially untouched. The measure used for this estimate is the difference between crust and mantle in the accumulation of the isotope neodymium-143, the decay product of the radioactive isotope samarium-147. This difference is caused by the crust and the depleted mantle having different samarium/neodymium ratios. This calculation yields a depleted mantle fraction of 30%. However, when we use an alternative measure for the same calculation, namely the concentration ratio of niobium to uranium (Nb/U), which differs by a factor of 8 between depleted mantle and continents, we find the depleted mantle fraction to be greater than 60%. Both of these results cannot simultaneously be correct. We therefore need a more complex Earth model, one that involves an additional "reservoir" with crust-like Sm/Nd but mantle-like Nb/U. We model this as an ancient ocean crust, which was buried and may now be hidden at the base of the mantle because of its high density. The bottom line is that nearly the entire mantle, not just its uppermost layer, was involved in making our continents. A buried ancient ocean crust might well explain the large density/temperature anomalies recently discovered at the base of the mantle by seismologists.

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Abstract

Most previous efforts to characterize the size and composition of the upper mantle, the source of mid-ocean ridge basalts (MORBs), have assumed that this MORB source is the residue of continental crust extraction. The use of Nd isotopes to model this process led to the near-consensus that the “depleted MORB reservoir” is more-or-less confined to the upper mantle (above 670 km, ~30% of the mantle), with a severe degree of depletion of incompatible elements, leaving the lower mantle in a more primitive state. Here, we reassess the mass and composition of the mantle reservoir depleted by continental crust extraction. We initially apply simple mass balance considerations, using alternatively ε(Nd) and “canonical” (Nb,Ta)/U tracers, to a conventional three-reservoir silicate Earth consisting of primitive mantle, continental crust, and depleted mantle. The (Nb,Ta)/U tracer yields a ‘depleted reservoir’ exceeding 60% by mass of the total mantle (X(DM) > 0.6) with average ε(Nd) ≤ 3, whereas the ε(Nd)-based mass balance, using $\varepsilon(\mathrm{Nd})_{\mathrm{MORB}} = 8.5$, yields a “depleted reservoir” of X(DM) ≤ 0.3. This discrepancy requires additional processes/reservoirs that impact the fractionation of Sm/Nd in the depleted mantle. Simple segregation of enriched OIB sources is shown to be insufficient. Permanent sequestration of a fourth, early-enriched, mafic reservoir (EER), leaving behind an early-depleted reservoir (EDR) can resolve the dilemma. Segregation of the present-day continental crust from EDR generates a moderately depleted, “residual-mantle” reservoir (RM), which occupies 80-98% of the total mantle (X(RM) = 0.8-0.98). This leads to concordant results for the two crust-mantle mass balances.
(Word count: 249)

1. Introduction

The discovery of the trace-element depleted nature of the mantle region underlying mid-ocean ridges has been one of the fundamental contributions of geochemistry to the understanding of the differentiation of our planet. The first clear indication of this was probably the particularly unradiogenic isotopic composition of strontium and low abundances of highly incompatible elements (Gast, 1968; Hart, 1971). But the actual degree of depletion could only be assessed when Nd isotopes were shown to be correlated with Sr isotopes, which allowed DePaolo and Wasserburg (1976) and O'Nions et al. (1977) to tie the degree of depletion to a chondritic reference frame. This had not been possible on the basis of Sr isotopes alone, because Earth's bulk Rb/Sr and $^{87}Sr/^{86}Sr$ ratios are not chondritic. The fact that the Sr-Nd isotope correlation of the oceanic mantle connects to the composition of the continental crust immediately led to the idea that the depletion of the MORB source is complementary to the enrichment of the continental crust. O'Nions et al. (1979) and Jacobsen and Wasserburg (1979) evaluated the size of the depleted mantle reservoir, using models of global crust-mantle Nd-Sr isotopic evolution, and found that this reservoir constitutes only between 20 and 50% of the mantle mass. This interpretation was seemingly substantiated by Hofmann (1988) who showed that the complementary patterns of isotopes in MORB sources and continental crust also appear to hold true for the entire suite of trace element abundances commonly used in so-called spidergrams.

At the time, the main controversial aspect concerned the importance of ocean island basalts (OIBs) in the global mass-balance. Wasserburg and DePaolo (1979) suggested that OIBs are derived from an undifferentiated, "primitive" reservoir in the lower mantle, and this model appeared to be consistent with primordial ^{3}He in at least some OIBs (e.g. Kurz et al., 1982). Indeed the original Nd-Sr 'mantle array' of DePaolo and Wasserburg (1976) and O'Nions et al. (1977) could be explained as mixing between primitive lower mantle sources of OIB and the upper mantle source of MORB. However, considering Pb isotopes, Sun and Hanson (1975) and Zindler et al. (1982) showed that the OIB sources had more complex histories. Hofmann and White (1980, 1982) proposed that OIB sources are dominated by recycled oceanic crust that has been stored in the mantle for geologically long periods of time, and Christensen and Hofmann

(1994) showed that this recycling process can match a large part of the observed Pb and Nd isotopic variations of MORBs and OIBs.

Subsequently, using trace elements, Hofmann et al. (1986) found that most OIBs have similar or identical Nb/U (and Ce/Pb) ratios as MORBs, which are different from, and complementary to, the continental crust. This further confirmed that OIBs cannot be derived from a primitive mantle reservoir. The Nb/U and Ce/Pb ratios became subsequently known as "canonical" ratios, because their value is essentially invariant in MORBs and most OIBs, independent of the enrichment or depletion of the absolute Nb and U, or Ce and Pb, concentrations respectively, over more than two orders of magnitude. Figure 1 is an updated illustration of the relationship of Nb/U between global MORB (using the MORB segment averages given by Gale et al., 2013), continental rocks including 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 a proxy for overall incompatible-element enrichment/depletion. Figure 1 shows that, in contrast with most other trace element ratios, Nb/U (as well as Ce/Pb) can efficiently discriminate between continental and intra-oceanic basalt sources. Radiogenic isotope ratios are inherently less suitable for this purpose, because their parent and daughter elements invariably have different partition coefficients during mantle melting, and therefore parent/daughter ratios can be fractionated by both continental and intra-oceanic melting processes. Hofmann et al. (1986) argued that both MORB and OIB sources are residual to the continental crust, and both must have been subsequently differentiated by an additional process such as the segregation and storage of oceanic crust. Hofmann (1989) estimated the size of the overall mantle residue from continent extraction to be greater than 50%. He did not, however, attempt to estimate the mean composition of this reservoir, nor did he address the question to which extent the composition of the depleted MORB-source reservoir *sensu stricto* has been affected by this additional differentiation. Campbell (2002) explored in more detail the differences between extracting continental and oceanic crust on the Nb/U and Sm/Nd ratios of this mantle residue from continent extraction.

He concluded that extraction of continental crust accounts "for only about one third of the increase in the Sm/Nd seen in modern MORB-type basalts."

Subsequently, two seminal studies focused specifically on evaluating the composition of the depleted MORB mantle (DMM). Salters and Stracke (2004) realized that the relationship between the continental crust and the depleted MORB mantle is "not strictly complementary," but did not further evaluate the potential effect of other reservoirs, such as OIB sources, on the overall mass balance between the depleted MORB source (DMM) and the continental crust. These authors used Hf, Nd and Sr isotopes of depleted MORB to infer the respective parent-daughter ratios and element concentrations of DMM. This calculation requires knowledge of the temporal evolution of the depletion process, and their preferred average differentiation age, 2.2 Ga, essentially coincides with what was thought to be the average age of the present-day continental crust. Following a somewhat different approach, Workman and Hart (2005) used REE data of clinopyroxenes from oceanic peridotites to demonstrate a correlation between ln(Sm) and ln(Nd). By intersecting this correlation line with the locus of Sm/Nd = 0.411, derived from the Nd isotopic composition of MORB and a model of continuous continent extraction, they derived a depleted mantle composition significantly more depleted than the one inferred by Salters and Stracke (2004). From the perspective of the present paper, it is important to note that the Nd isotopic composition of MORB and the age of crust-mantle differentiation play crucial roles in both of the studies just discussed. The decisive effect of the extraction of the continental crust on the composition of the MORB source was also a basic assumption of the global chemical differentiation model of Hofmann (1988).

Starting in 2005, the traditional interpretation of the terrestrial Nd-isotopic evolution has been in a state of turmoil, because Boyet and Carlson (2005) demonstrated that terrestrial $^{142}Nd/^{144}Nd$ ratios are higher than their chondritic counterparts by about 20 ppm. ^{142}Nd is the daughter product of the short-lived, now extinct nuclide ^{146}Sm, and these new results appeared to require that the observable terrestrial Sm/Nd ratio has increased from its initial chondritic value, presumably by some kind of very early, global differentiation process that generated an "early-enriched reservoir" (labeled EER) possessing lower-than-chondritic Sm/Nd, and an "early-depleted reservoir" (labeled EDR) possessing higher-than-chondritic Sm/Nd. All known terrestrial samples were derived from the EDR, and this implied that the enriched EER is either permanently hidden deep in the Earth or lost from Earth altogether. We nevertheless mention this story here, because an early-enriched reservoir had previously also been proposed by Tolstikhin and Hofmann (2005) on the basis of noble gas abundances in mantle-derived basalts, which demonstrate the survival of a primordial noble gas reservoir presumably located at the base of the mantle. More recent research has suggested that the observed terrestrial $^{142}Nd/^{144}Nd$ excess is nucleosynthetic in origin and is therefore not caused by non-chondritic $^{147}Sm/^{144}Nd$ or $^{143}Nd/^{144}Nd$ ratios (e.g. Burkhardt et al., 2016). If this is correct, the ^{142}Nd data no longer require the formation of an EDR. In the course of this present paper, we will be forced to return to the concept of an early EER-EDR differentiation, though on the basis of completely different evidence.

In this paper, we apply a simple mass balance approach, as originally set out by Davies (1981) to evaluate the proportions of the present-day mantle reservoirs by their isotopic compositions. This method has the advantage of being independent of any knowledge or assumptions about the timing of Earth's differentiation. It can be applied using any chemical or isotopic parameter, including isotope ratios or chemical ratios that discriminate effectively between the different reservoirs concerned. We initially use the canonical ratios Nb/U and Ta/U, because these ratios are distinctive and well-defined for each of the main reservoirs, primitive mantle, continental crust, and depleted mantle. We then compare these initial results derived from the (Nb,Ta)/U parameters with the analogous calculation employing ε(Nd).

While the two analogous calculations should yield consistent results, in fact, they yield dramatically inconsistent results, and to explain this discrepancy, we argue that the Sm/Nd ratio, and consequently the ε(Nd) value, of the MORB mantle *sensu stricto* is controlled not only by extraction of continental crust but also by extraction (and storage) of oceanic crust. It will be seen, however, that simple inclusion of a present-day OIB source reservoir in the mass balance is insufficient to resolve the overall discrepancy. Instead, an additional, hidden reservoir is required, which contains primitive (Nb,Ta)/U ratios but fractionated Sm/Nd (and Lu/Hf) ratios. Such an "early-enriched" reservoir (EER) could have been generated by segregating an early-formed mafic crust. Whether this reservoir is permanently stored in the deep mantle or ejected from Earth by a collisional erosion process during late accretion is immaterial to the mass balance. We assume that the complementary early-depleted reservoir (EDR) will be homogenized and is 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) presented initially. We will show that under such conditions the mass balance calculations can yield concordant results, whereby the residual mantle occupies more than 80% of the total mantle, and its incompatible trace element budget is only moderately depleted. A cartoon at the end of this paper summarizes the final model.

We will 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 conventional 3-reservoir Earth consisting of CC, PM, and DM. DM is the simple chemical complement to the continental crust.
- EER - Early-enriched reservoir (= early-formed mafic crust), either permanently stored in the deep mantle or possibly lost by collisional erosion during late accretion).
- 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 mantle consisting of an early-enriched reservoir (EER), an early-depleted reservoir (EDR), continental crust (CC), and a residual mantle reservoir (RM) formed by extraction of CC from EDR.

2. Data assessment

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

Before presenting the actual mass balance calculation, it is necessary to reassess the “canonical” trace element data first presented by Hofmann et al. (1986), using modern, high-quality trace element data of oceanic basalts. The original evaluation of the Nb-U relationships proposed by Hofmann et al. (1986) was based on just thirty MORB samples and a similar number of OIB samples. It has since been criticized on the grounds that diagrams such as Nb/U versus Nb, in which the two variables employed are not independent, are inherently unsuitable for a statistical assessment of the constancy of the Nb/U ratios (Sims & DePaolo, 1997). These authors argued correctly that, on statistical grounds, a log Nb vs log U plot is better suited for this purpose. Such log-log plots had been used extensively by Wänke et al. (1973) and also by Hofmann and White (1983). A slope of 1.0 on such a plot means that the Nb/U ratio is independent of the absolute concentration of either Nb or U, and under this condition the Nb/U ratio is also identical to that of the basalt sources, as originally proposed by Hofmann et al. (1986). The statistical "correctness" notwithstanding, the representation originally chosen by Hofmann et al. (1986) has the advantage of displaying the uniformity of a trace element ratio in a more intuitive way. Figure 2 is an example of this; it displays Nb/U, Nb/Th, Ta/U, and Nb/La as functions of the absolute Th concentration in the set of about 600 MORB glasses analyzed by Jenner and O'Neill (2012a). The Th concentration serves as a proxy for the relative enrichment/depletion of any highly incompatible element over two orders of magnitude. This shows that Nb/La, unlike Nb/U and Ta/U, should not be used as a canonical ratio, because its value increases systematically by about a factor of three, as the Th value increases by a factor of about 100. Using the statistically more appropriate log-log approach, Arevalo and McDonough (2010) found that their global suite of MORB data yielded a log Nb vs log U slope that deviated slightly but significantly from unity. Because of this, they rejected the use of Nb/U as a canonical ratio for the purpose of characterizing the mantle source(s) of MORBs.

To address this issue we reexamine the question of which trace element ratio in oceanic basalts reflects the mean composition of the residual mantle most closely and can, at the same time, be used as the most effective discriminator between continental crust and residual mantle. For this purpose, we use three recently published, high-quality, global data sets for hundreds of MORB samples, usually fresh basalt glasses, by Arevalo and McDonough (2010), Jenner and O'Neill (2012a), and Gale et al. (2013). We argue that the deviation of the slope of a log-log correlation from unity need not necessarily be smaller than the statistical uncertainty of this deviation, in order for such a ratio to be "canonical" in the sense that it can be used as tracer of source composition. Indeed, it is exceedingly unlikely that two chemical elements should have exactly identical bulk partition coefficients in any setting of mantle melting. The relevant question is therefore not whether the bulk partition coefficients of two elements are identical within error, but how large an error is introduced by small but inevitable differences in the respective partition coefficients. In the case of tholeiitic melting with melt fractions well in excess of 1%, the effect of melting on the ratio of two highly incompatible elements is likely to be quite small. For example, $Th/U \leq 1.02$ in MORB-type batch partial melts at $F \geq 0.05$ correspond to a source ratio of $Th/U = 1.0$ and bulk partition coefficients $D(Th) = 0.00167$ and $D(U) = 0.00247$ (Ds from Salters & Stracke, 2004).

For the purpose of characterizing the mean composition of a source reservoir, more caution is in order if the mantle source ratios vary slightly as a function of absolute depletion or enrichment, because the true mean value of the mantle may not be identical to the mean value of the rocks sampled. However, the problem can still be evaluated by using more than one element ratio and bracketing the results. Thus, rather than simply testing the Nb/U ratio proposed thirty years ago, we determine which of a series of similarly incompatible elements is closest in partitioning behavior to Nb, and we repeat this exercise for Ta. These evaluations are shown in Figures S1 and S2 (Supporting Information), which illustrate examples of the log-log correlation plots (Fig. S1) and the systematic relationships of the slopes of these log-log plots (Figs. S2). Table S1 (Supporting Information) lists the relevant slopes and uncertainties. The results for three different global MORB datasets are remarkably consistent; they demonstrate that Nb/U and Ta/U bracket the ideal log-log slope of 1.00. We therefore use both of these ratios to bracket our mass balance calculations. Table S2 (Supporting Information) lists the mean values of the various ratios to be used in the mass balance calculations further below.

Our quantitative evaluation relies exclusively on global data sets for MORB, and we exclude data for ocean island basalts (OIBs) because some OIB sources, specifically the EM-types, are clearly “contaminated” by recycled continental material (e.g. Jackson et al., 2007). In addition, Nb/U and Ta/U data for OIBs are generally somewhat more variable than MORB data, partly because most OIB are subaerial and subject to alteration, which commonly affects U concentrations rather severely.

The relationships seen in Figure S2 (Supporting Information) may be translated into a sequence of increasing compatibility of Ba < Th < Nb < U < Ta <K < La. Although none of the slopes conforms to the exact value of unity, the element pairs Nb – U and Ta – U come remarkably close, and the "best match" for uranium would be an element with enrichment-depletion properties between those of Nb and Ta. Table S2 (Supporting Information) 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. For the purpose of this paper, we will use values obtained by Gale et al. (2013), because the authors of this paper took special care to obtain the best representative average composition of the global mid-ocean ridge system.

To assess the question whether OIBs in general should be considered to be derived from the same residual reservoir as MORBs, and in order to avoid the difficulties introduced by U alteration, we plot the chemically more "robust" Nb/Th ratios for both global MORB and a large number of OIBs and oceanic plateaus. Figure S3 shows that Nb/Th ratios of OIBs are overwhelmingly part of the same population as MORBs in having Nb/Th ratios higher than primitive-mantle values, analogous to Nb/U ratios. As shown in Figures 2 and S2, the Nb/Th data are less reliable for quantitative evaluations of the silicate Earth mass balance because the slope of the log Th vs. log Nb correlation deviates from unity more significantly than is observed for log U vs log Nb or log Ta. Thus, although the Nb/Th ratio of a given basalt is likely to reflect its source ratio quite closely, it is difficult to know the mean Nb/Th ratio of the bulk residual mantle that incorporates both MORB and OIB sources.

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

The parameters Nb/U and Ta/U, used in this paper to evaluate the crust-mantle mass balance, will be useful only if their values are known for the various reservoirs. For the bulk silicate Earth (commonly referred to as BSE), the traditional assumption has been that Nb, U, and Ta are all refractory lithophile elements, which are present in chondritic relative abundances, resulting in BSE ratios for Nb/U = 32.4 and Ta/U = 1.82 (McDonough & Sun, 1995), corresponding to a Nb/Ta ratio 17.8, then thought to be the best chondritic value. More recently, it has become increasingly clear that nearly all terrestrial rock reservoirs have Nb/Ta ratios substantially lower than 17.8. Moreover, Münker et al. (2003) redetermined the chondritic value at Nb/Ta = 19.9, using new, high-precision analyses. These authors estimated the value for bulk silicate Earth to be as low as Nb/Ta = 14.0. This was in part based on a rough correlation between Nb/Ta and Zr/Hf in the various rock reservoirs. Most recently, Münker et al. (2017), using additional high-precision data on meteoritic silicates, metals and troilites, confirmed an earlier suggestion by Wade and Wood (2001) that the missing niobium may reside in Earth's core. In addition, they showed that niobium is rather easily partitioned into sulfide phases at low pressures and at moderately low oxygen fugacities. From these observations they inferred that much of the niobium deficiency in the silicate Earth was generated in asteroidal bodies prior to Earth accretion. Consequently, the apparent correlation between terrestrial Nb/Ta and Zr/Hf should no longer be used to infer the specific Nb/Ta value of BSE (C. Münker, 2017, personal comm.). Currently available high-precision Nb/Ta ratios are available for MORB (average 14.5 ± 1.2, Büchl et al., 2002), a variety of OIB (average Nb/Ta = 15.9 ± 0.6, Pfänder et al., 2007), and several Archean greenstones (Nb/Ta = 15.5 ± 0.7, C. Münker et al., 2003). The similarity of these ratios in a large variety of mantle-derived volcanic rocks is consistent with the interpretation that the BSE Nb/Ta ratio lies between 15 and 16. It will be seen below that, by using a Nb/U = 27.34, reduced from McDonough and Sun's (1995) value of 32.41 and corresponding to a reduction of Nb/Ta from 17.78 to 15.0 for the bulk silicate Earth, we obtain concordant results when calculating the amount of depleted mantle complementary to the continental crust from Nb/U and Ta/U ratios in mantle and crust.

3. Mass balance for a 3-reservoir silicate Earth

3.1. Equations and input parameters

Following the formulation of Davies (1981), the mass balance in a simple, three-reservoir silicate Earth is given by equations (1) to (3), where X is the mass fraction of a given reservoir, R is a property such as an isotopic or chemical 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 reservoir, and depleted mantle reservoir, respectively:

$$X_{dm} + X_{pm} + X_{cc} = 1 \quad (1)$$

$$X_{dm}\, C_{dm} + X_{pm}\, C_{pm} + X_{cc}\, C_{cc} = C_{pm} \quad (2)$$

$$X_{dm}\, C_{dm}\, R_{dm} + X_{pm}\, C_{pm}\, R_{pm} + X_{cc}\, C_{cc}\, R_{cc} = C_{pm}\, R_{pm} \quad (3).$$

The solution of these equations is:

$$X_{dm} = \frac{X_{cc}\,C_{cc}\,(R_{dm} - R_{cc})}{C_{pm}\,(R_{dm} - R_{pm})} - X_{cc} \quad (4),$$

which is then used to evaluate the composition of the residual reservoir:

$$C_{dm} = \frac{C_{pm}\,(X_{dm} + X_{cc}) - X_{cc}\,C_{cc}}{X_{dm}} \quad (5).$$

Here we specify $(Nb/U)_{dm}$ and $(Ta/U)_{dm}$ for R_{dm}, in order to evaluate the mass fraction of the depleted mantle reservoir, X_{dm}, and the trace element concentrations, C_{dm}, in this reservoir. Note that the version of equation (4) given by Hofmann (2003, 2014) is in error, because the final term, $-X_{cc}$,, is missing from equation (13) in Hofmann (2003) and equation (14) in the updated Hofmann (2014) version. Quantitatively, the effect of this error is very small because the value of X_{cc} is so small (= 0.006).

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 to take account of the Nb deficiency in the bulk silicate Earth (see discussion above). 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); see also Table S3 . 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 for our estimates of the residual mantle composition. 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 only minor scatter in the mass balance results seen in Fig. 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 an undepleted, or "primitive" lower mantle. In its simplest form, this model has largely been laid to rest by the findings of seismic tomography and geochemistry. But it can nevertheless serve as a starting point in evaluations of the mantle reservoir involved in forming the continental crust. It will be seen further below, after our reevaluation of the analogous mass balance using Nd isotopes, that this model is in fact 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, reservoir.

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

We initially compute a preliminary mass fraction of the depleted mantle, X_{dm}, from equation (4) using the "conventional," chondrite-based BSE Nb/U ratio of 32.4 and Nb/Ta of 17.78 from McDonough and Sun (1995). Figure 3 shows that the depleted mantle fraction calculated using this Nb/U value (gray symbols) is quite different from equivalent calculation based on Ta/U (that is using values of 1.82 for the BSE (McDonough & Sun, 1995) and 3.088 for average MORB (Gale et al., 2013)), which yields substantially lower depleted mantle fractions (blue symbols). In addition, both calculations depend strongly on the assumed U content of the continental crust, so that for crustal U abundances greater than about 1.1 ppm, the mass fraction of the depleted mantle calculated from Nb/U would exceed unity, which is physically impossible. As we explained in the previous section, this discrepancy between the Nb/U and Ta/U-based results is almost certainly caused by the failure to take the subchondritic Nb content of BSE into account. As a next step, we therefore reduce the BSE value of Nb from 0.658 to 0.555 ppm, corresponding to a reduction of the BSE Nb/Ta ratio to 15.0 (see previous section). This reduction then leads to amounts of depleted mantle that are essentially concordant with the Ta/U-based results (Fig. 3, red symbols). Overall, Figure 3 shows that, for the simple three-reservoir model, the mass of the depleted mantle amounts to 60 to 80 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 of 25 to 30 %.

3.3. Comparison with mass balance for the 'depleted mantle' reservoir based on Nd isotopes.

We now address the question why essentially all the earlier estimates yielded a much smaller size of the depleted mantle reservoir of 20 to 50% (Davies, 1981; Jacobsen & Wasserburg, 1979; O'Nions et al., 1979), compared to the 60 to 80% indicated by our present mass balance based on canonical ratios. To evaluate this discrepancy, we now use Nd isotopes with the same three-reservoir Earth model and the same mass balance (eq. (1) to (5) as above, as was originally proposed by Davies, 1981). Thus, we simply replace the parameters Nb/U and Ta/U by ε(Nd). We reiterate that this calculation uses the implicit assumption that the depleted reservoir is generated exclusively by extraction and isolation of the continental crust, thus neglecting other possible differentiation mechanisms such as extraction of OIB sources. We update the parameters for MORB, primitive mantle and continental crust used by Davies (1981) to more current values. We use a value of ε(Nd) = +8.5 for MORB (the "ALL MORB" average of Gale et al., 2013), and Nd concentrations of 20 ppm for the continental crust (Rudnick & Gao, 2003) and 1.25 ppm for the primitive mantle (McDonough & Sun, 1995). A difficulty arises when choosing the ε(Nd) value of the average continental crust, because the current literature gives no authoritative estimates of this. Chauvel et al. (2014) use loess data to estimate the present-day upper continental crust at ε(Nd) = -10.3 ±1.2, similar to the value of ε(Nd) = -11.4 ±4 obtained by Goldstein et al. (1984) for major river systems and atmospheric dust. However, one of the problems with assessing the Nd isotopic composition of the bulk crust lies in the fact that this parameter depends strongly on the age of the crust. Taking loess, major rivers, and atmospheric dust values as representative of the average upper crust assumes that these are unbiased samples of the upper crust, which may not be the case. For example, major rivers preferentially sample mountain belts and under-sample shield regions, introducing a bias toward younger-than-average continent. Loess deposits sourced from mountain glaciers would have a similar bias. In addition, the lower continental crust is often considered be more mafic than the upper crust, or older. To our knowledge, the only attempt to evaluate the average ε(Nd) of the lower continental crust was based on limited xenolith data (Rudnick, 1990; Rudnick & Goldstein, 1990). For example, the mean value for Archean shales from the Barberton Greenstone belt is ε(Nd) = -27 ± 4 (Garçon et al., 2017). Thus, if the lower crust contains a greater proportion of Archean rocks than does the upper crust, the estimate derived from the loess-river-dusts might be significantly biased. We therefore allow a wide range of crustal ε(Nd) values, from -10 to -17. Figure 4 shows the results for the three-reservoir model using Nd isotopes, in terms of the mass fraction of a complementary depleted mantle reservoir as a function of the ε(Nd) value of the bulk continental crust. Thus, if the upper crustal value of ε(Nd) = -10 applies to the bulk continental crust and the depleted mantle has an average MORB composition with ε(Nd) = 8.5, the mass fraction of the mantle reservoir is quite small, X_{dm} = 0.2. But even if the bulk crust has an ε(Nd) value of -17, the mass fraction of the depleted mantle with ε(Nd) = +8.5 is still only about X_{dm} = 0.3. Caro (2011, Fig. 1) arrived at essentially the same conclusion on the basis of simple crust extraction models and their effects on mantle ε(Nd).

We examine this result by calculating the composition of the depleted mantle from equation (5) using the mass fraction of the depleted mantle and the estimated composition of the continental crust. Figure 5 shows immediately that it is not possible to extract present-day continental crust of the composition given by Rudnick and Gao (2003) or McLennan et al. (2006) from a mantle mass fraction as small as X = 0.3, because it would require several of the most highly incompatible elements in the depleted mantle to have negative concentrations in order to satisfy the mass balance with the crust, which is of course physically impossible. This provides independent confirmation that the "classical," Nd-isotope based assessments of the crust-mantle balance are inconsistent with current estimates of the composition of the continental crust.

Another feature of the conventional small volume – highly depleted mantle is examined in Fig. 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 of Gale et al. (2013), Fig. S4 shows that a melt fraction of 3% would be required to generate ALLMORB from such a Workman-Hart-type mantle 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).

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

We recall that the mass balance based on ε(Nd) uses only the MORB source as the sole depleted complement of the continental crust, whereas the mass balance based on (Nb, Ta)/U also includes the bulk of the OIB and oceanic plateau sources, which, on average, have significantly lower ε(Nd) values than the MORB source reservoir. Such an internal differentiation of the depleted mantle into more enriched OIB sources and correspondingly more depleted MORB sources is expected to be the result of ocean crust recycling and extended storage, as was proposed by Hofmann and White (1982). This process was also invoked by Hofmann et al. (1986) to explain the observed heterogeneity in incompatible-element enrichment/depletion coupled with the absence of systematic differences in Nb/U in MORB and OIB. In any case, the two mass balance calculations are not strictly equivalent, and it might therefore be possible to resolve the differences in the two mass balances by including the OIB source reservoir(s) in the mass balance calculation for ε(Nd). Unfortunately, the ε(Nd) of the bulk depleted mantle (including both MORB and OIB sources) is poorly constrained. Consequently, we explore this possibility by solving equation (4) for a range of potential ε(Nd) values that might represent the combined MORB-OIB source reservoir. Figure 4 shows that for a range of crustal ε(Nd) values of -10 to -17, which includes the crustal estimates given by Goldstein et al. (1984), Goldstein and Jacobsen (1988), Rudnick (1990), and Chauvel et al. (2014), the bulk residual mantle would have to have an ε(Nd) value ≤ 3.5, in order to be consistent with a mass fraction of 0.8 ≥ X_{dm}(Nb,Ta/U)≥ 0.6. As will be seen below, such a low ε(Nd) value is inconsistent with any plausible combination of observed ε(Nd) values of MORBs, OIBs and oceanic plateaus.

Table S4 and Figure 6 present an informal compilation of ε(Nd) values for OIBs from major hotspots and for oceanic plateaus. We selected the 28 hotspots listed by Sleep (1990) for which there are adequate Nd isotope data. The hotspot data show a mean value of ε(Nd) = 4.37 ± 2.27 (1 std deviation), corresponding to a standard error of ± 0.43 for 28 hotspots. The Pacific oceanic plateaus yield a mean value of ε(Nd) = 5.8. From this it seems reasonable to infer that the bulk ε(Nd) value of the combined MORB-OIB mantle should be less than 8.5, the average MORB value of (the average MORB value of Gale et al., 2013), but significantly greater than 4. Therefore, a simple internal differentiation of the "bulk depleted" mantle into a more depleted MORB reservoir and a relatively more enriched OIB-oceanic plateau source reservoir cannot reconcile the mass balance based on ε(Nd) with the one based on (Nb,Ta)/U (compare Fig. 4: ε(Nd) = 4, brown dashed line, only gives X_{dm} of ~33-60%). This also reinforces Campbell's (2002) argument (based on partial melting considerations) 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.

We thus conclude that these considerations constitute compelling evidence against any simple three-reservoir silicate Earth model, whereby a 'depleted mantle', which may include OIB- and oceanic-plateau sources as well as MORB mantle, is the sole depleted complement of the continental crust. In order to reconcile the (Nb,Ta)/U-based - and the ε(Nd)-based mass balances, we require an additional reservoir with a low Sm/Nd ratio but (approximately) primitive Nb/U and Ta/U ratios. This reservoir is inaccessible to being sampled by melts erupted at the surface. Its segregation must have increased the ε(Nd) value of the observable mantle without significantly affecting its Nb/U and Ta/U ratios. In other words, it must have been formed prior to the segregation of the present-day continental crust. We suggest that an early-formed and subsequently sequestered mafic crust would meet these requirements. We will explore this in more detail further below.

In summary, the increase of Sm/Nd reflected by the Nd isotopic composition of the MORB source is caused by at least two processes, (1) removal of continental crust and (2) removal of other enriched material, such as a primordial mafic crust. Because of this additional differentiation process, the small mass fraction obtained for the "depleted" mantle derived from the traditional 3-reservoir, Nd-isotope based mass balance represents a significant underestimate of the actual mass fraction of the mantle complement to the continental crust.

4. The four-reservoir silicate Earth

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

We now explore the consequences of the proposed hidden reservoir, the need for which has been explained above. We suggest that this reservoir is generated by the formation and permanent sequestration of an ancient, possibly primordial, mafic crust in a manner similar to what has previously been suggested and labeled "EER" by Boyet and Carlson (2005) on completely different grounds, namely the elevated, non-chondritic ^{142}Nd abundances of the bulk silicate Earth. This mafic crust resembles oceanic crust in that its Sm/Nd and Lu/Hf ratios are lower than primitive, while at the same time retaining primitive (BSE) Nb/U and Ta/U ratios. Removal of such mafic material will generate an early-depleted reservoir, the EDR in the nomenclature of Boyet and Carlson (2005), with elevated Sm/Nd and ε(Nd) and a moderate degree of depletion of all incompatible elements. We model this using a simple batch melting approach with a melt fraction of F = 0.1 and bulk partition coefficients appropriate for spinel lherzolite proposed by Salters and Stracke (2004). We then sequester a small amount of this partial melt to create the EER, leaving behind a large, moderately depleted mantle reservoir, labeled EDR. For the purpose of this discussion, we “aim” for an EDR having a present-day ε(Nd) = +3.5. This can be achieved, for example, by an EER having a mass fraction X_{EER}= 0.02 and produced by batch melting with F = 0.1 (Fig. 7). Alternatively, such an EDR can also be generated by a moderately higher melt fraction of F = 0.12 for generating the EER, and a corresponding increase in the amount of sequestered EER (X_{EER} = 0.03). Using the partition coefficients suggested by Workman and Hart (2005), a similar result can be achieved by choosing the combination of F = 0.10 and X_{EER} = 0.03. We then calculate the complete trace element composition of this EDR. Figure 8 shows that in such an early depleted mantle, the concentrations of the most highly incompatible elements are reduced to values ranging between roughly 70 and 80% of the original BSE values. We note that this degree of depletion is considerably more moderate than a reduction of U and Th by fully 50% as a result of “collisional erosion suggested by O’Neill and Palme (2008).

Figure 9 evaluates subsequent Nd-evolution models for one of the above EDR models, corresponding to partition coefficients of Salters and Stracke (2004) and values of F = 0.1 and X_{EER} = 0.02. This raises the $^{147}Sm/^{144}Nd$ ratio of the complementary EDR from its chondritic value, 0.1960 (Bouvier, 2008), to a value of 0.2019, and generates a present-day ε(Nd) = 3.49 of the EDR. This is the new base line of the Nd isotope evolution, from which the continental crust is differentiated. The subsequent extraction of the present-day continental crust is shown, for simplicity, as a single event at 2.0 Ga intended to broadly represent the mean age of the present-day continental crust (Figure 9). The value of 2.0 Ga compares with mean age estimates of 1.82 Ga by Chauvel et al. (2014), 2.0 Ga by Goldstein et al. (1984). and 2.1 Ga by (e.g. Goldstein & Jacobsen, 1988) , We use the estimates of the bulk Sm and Nd concentrations of the continental crust of three different studies (Hacker et al., 2015; McLennan et al., 2006; Rudnick & Gao, 2003) to represent the range of likely isotopic compositions of the present-day residual mantle. Given the variability of these evolution lines, we conclude that this type of Nd isotope evolution is consistent with the observed isotopic composition of a “residual mantle” that generates both MORBs and OIBs.

4.2. Mass balance of the four-reservoir Earth

We now use the proposed EDR as a new starting composition to recalculate the mass balance of a new three-reservoir system encompassing EDR, continental crust, and residual mantle (RM). Overall, this actually represents a four-reservoir system in which one reservoir, the EER, has been estimated by an *a priori* forward model, designed to reconcile the two independent mass balances for the remaining three reservoirs (i.e. those based on Nd isotopes and on (Nb,Ta)/U ratios). Figure 10 shows that size of the residual reservoir, X_{RM} (=mantle residue after extraction of present-day continental crust from the EDR), occupies between 80 and nearly 100% of the mantle, depending on the specific U content of the crust within our preferred range of U = 1.1 and 1.3 ppm, using the MORB value of Nb/U = 46 for the combined MORB-OIB source to represent the composition of the entire residual mantle. This range thus includes possible cases where the entire silicate Earth is “residual” except for the 2 to 3% required for the EER and the 0.006% taken up by the continental crust, as well as cases where up to nearly 20% of the silicate Earth may still have its original EDR composition. Figure 10 also shows the respective results for cases where the bulk residual Nb/U might be different from the MORB value of 46. This range of Nb/U values reflects an approximate uncertainty introduced by the inclusion of the OIB sources. The results for Nb/U = 42 and 50 shown in Fig. 10 demonstrate that the residual mantle reservoir still takes up more than 70% of the total mantle even if Nb/U is as high as 50, given the same range of crustal U values.

The composition of the final residual mantle after extraction of the present-day continental crust for this system of the four reservoir Earth is calculated using equation (5). All three crustal estimates lead to remarkably similar compositions of the residual mantle, as shown in Figure 11 and listed in Table 1. In detail, the most highly incompatible element abundances vary somewhat, depending on the specific crustal abundances of these elements given by the various authors (Hacker et al., 2015; McLennan et al., 2006; Rudnick & Gao, 2003), but all of these element patterns are significantly less depleted than the depleted mantle estimates given by previous workers (Salters & Stracke, 2004; Workman & Hart, 2005), shown here for comparison. Aside from this lower degree of depletion, the magnitude of the negative Pb anomaly is more variable and less extreme than those given in previous estimates (Salters & Stracke, 2004; Workman & Hart, 2005). This is most likely the result of the greater uncertainty in the Pb concentration in the continental crust relative to those of the REE abundances in the various estimates. The more important point, however, is that all of the U and Th abundances of the new are residual mantle estimates are three to four times higher than those given by Workman and Hart (2005) and about two to three times higher than those given by Salters and Stracke (2004). In particular, the abundances of Th and U are roughly 40 to 50% of their respective primitive-mantle values, rather than 10 to 20% as previously estimated. The earlier, much more extreme depletions were direct results of the assumption that the depleted MORB source is the sole residue of the continental crust.

5. Summary and concluding discussion

We have reevaluated the global crust-mantle differentiation of the traditional three-reservoir silicate Earth consisting of continental crust, depleted mantle, and primitive mantle reservoirs. The mass of the depleted reservoir exceeds 60% of the total mantle if we use Nb/U and Ta/U ratios as discriminants between continental crust and depleted mantle. The analogous result based on Nd isotopes (instead of (Nb,Ta/U)) yields a depleted reservoir mass of only 30%, if its ε(Nd) value is 8.5 (the current best MORB average), and still less than 50% if its ε(Nd) is as low as +4 (close to the OIB average). Thus, the three-reservoir model is unable to simultaneously account for both parameters used as measures of crust-mantle differentiation.

The conflicting mass balance constraints can be reconciled with a four-reservoir Earth model (Fig. 12) including an additional, early-enriched mantle reservoir (EER) and its complement, the early-depleted reservoir (EDR – Fig.12a). 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 is moderately depleted in incompatible elements, and it serves as a source for the continental crust (Fig. 12b). Nb/U and Ta/U ratios are fractionated during continent formation. The residue of continental crust formation is the “residual mantle”, which occupies at least 80% of the total mantle, and it may occupy all of it, except for the EER itself. This means that only 0 to 20% of the original EDR survives to the present day. The trace element composition of the residual mantle is not nearly as depleted as currently used estimates of “depleted”-mantle compositions (Fig. 11). The residual mantle reservoir has been further differentiated into more depleted MORB mantle (avg. ε(Nd) = 8.5) and slightly more enriched OIB sources (avg. ε(Nd) = 4.4; Fig. 12c) by intraoceanic melting and subduction processes, a subject not addressed in this paper. As discussed below, the EER and possible remnants of the EDR might reside in the present-day LLSVP.

The EER is likely to have originated as an early mafic crust characterized by a lower-than-primitive Sm/Nd ratio but primitive (Nb,Ta)/U ratios. It might thus be quite similar to that postulated earlier by Boyet and Carlson (2005) and Carlson and Boyet (2008) on the basis of ^{142}Nd isotopes, and by Tolstikhin and Hofmann (2005) on the basis of xenon isotopes; however, our present argument for its existence does not rest on the evidence of short-lived nuclides. Alternatively, our results are consistent with models of complete removal of an early mafic crust, such as has been proposed by O’Neill and Palme (2008) in their model of collisional erosion.

The mass balance as discussed here addresses only the presently existing mantle and crustal reservoirs; it does not address the question of what happened to potentially large amounts of early Archean continental crust, now vanished but widely thought to have existed at one time. In contrast with the EM-type OIBs, where the recycled continental materials are clearly recognizable by their correlated Nb/U and Ce/Pb and isotopic signatures, (e.g. Jackson et al., 2007), any vanished early Archean continental crust cannot be identified in this manner, and we must assume that this material has been sufficiently well rehomogenized with the residual mantle, so that it has become an indistinguishable part of it. In any case, while the fate of the early Archean crust is important for the understanding of crustal evolution, it is of no particular consequence for the narrower purpose of mass balance evaluations of the present-day crust and its mantle residue.

Finally, we briefly revisit the possibility that the Early Enriched Reservoir is located within the LLSVPs (Large Low Shearwave Velocity Provinces), as shown in our cartoon of mantle evolution (Figure 12). These lower-mantle provinces have been recognized and delineated relatively recently (e.g.Dziewonski et al., 2010; Garnero & McNamara, 2008), and their total mass has been difficult to evaluate, with estimates ranging from 2% (Burke et al., 2008) to 9% of the silicate earth (Cottaar & Lekic, 2016). Their ages are essentially unknown, but might well approach the age of the Earth. Most workers agree that the LLSVPs are compositionally different from the surrounding and overlying mantle rocks. Thus, it is 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) have proposed a geodynamic model whereby the lower portion of the LLSVP is primitive, whereas the upper portion consists of recycled basaltic crust. Although our simplified three-reservoir treatment does not specifically address these issues, it is certainly 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 material that is significantly younger and possesses elevated (Nb,Ta)/U ratios caused by the extraction of continental crust.

In conclusion, previously published ε(Nd)-based estimates of the size and composition of the residual, depleted mantle are systematically in error, because they assume the continental crust to be the sole complement of the MORB-source mantle. The actual continental-crust residue includes both MORB and OIB sources. We have shown that no simple 3-reservoir mantle model consisting of a 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. Specifically, the ε(Nd)-based mass balance leads to a gross underestimate of the size of the residual reservoir (<40%). Conversely, the (Nb,Ta)/U-based mass balance leads to a residual reservoir with substantially lower ε(Nd)-values (<3.5) than is observed in MORBs and OIBs.

The internal inconsistencies of the three-reservoir models can be resolved by introducing a fourth reservoir. Such a reservoir may have been formed by the permanent segregation of an early mafic crust (= early enriched reservoir, EER). This would cause an increased Sm/Nd ratio in the remaining mantle, here called "EDR" (= Early Depleted Reservoir), while Nb/U and Ta/U ratios of both EER and EDR would retain their BSE values, because this mafic crust was not "continental" in nature. Our recalculation of the subsequent crust-mantle differentiation yields a mass of the residual reservoir exceeding 80%, and possibly close to 100%. It is much less depleted in highly incompatible elements, in particular the heat producers Th and U, than given by traditional, 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 incompatible element enriched OIB sources and the more depleted MORB sources should be a subject of future investigations.

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Figure Captions

Fig. 1.

Nb/U vs. Th for mid-ocean ridge basalts (MORB), 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 for 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 Nb = 0.658 recommended by McDonough and Sun (1995), to account for the loss of Nb from the bulk silicate Earth compared to chondrites (see section on reassessment of the Nb-Ta-Th-U relationships in oceanic basalts).

Fig. 2

Nb/U, Ta/U, Nb/Th, and Nb/La versus Th concentrations in about 600 MORB glasses. Data from Jenner and O'Neill (2012a). This illustrates the essential property of "canonical" trace element ratios: They 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, and it is unsuitable as a "canonical" ratio.

Fig. 3.

Mass fraction of depleted mantle, X_{dm}, based on canonical ratios in a three-reservoir Earth model. X_{dm} is calculated from equ. (5) 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 uranium content assumed for the continental crust, U_{cc} . We use a variety of published crustal uranium estimates with a 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 0.555

is used, yielding Nb/U and Nb/Ta of 27.34 and 15.00 for the BSE (see text). By contrast, the dashed curve, using an uncorrected BSE abundance for Nb, displays a 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 given in the literature (Hacker et al., 2015; McLennan et al., 2006; Rudnick & Fountain, 1995; Rudnick & Gao, 2003; Taylor & McLennan, 1985) see Table S3 (Supplementary Information), where the different estimates mostly represent different assumptions about the lower crust composition.

Fig. 4.

Mass fraction of depleted mantle, X_{dm}, based on Nd isotope ratios in a three reservoir Earth model. Mass balance results are shown for a range of possible ε(Nd) values of mantle and crust. The range of acceptable crustal 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 the depleted mantle range from the average MORB value (ε(Nd) = 8.5) to lower, less depleted values that might represent an integrated depleted mantle reservoir incorporating both MORB and OIB sources, ε(Nd) = 5, 4, 3, 2. If the depleted mantle occupies a mass fraction of = 0.6 to 0.8 (blue shaded region), 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 (8.5), average OIB (4.4), and Oceanic plateaus (5.8); see also Fig. 6.

Fig. 5

Three-reservoir mass balance based on MORB ε(Nd) yields impossible results: Depleted mantle compositions calculated from the mass balance equation (5), 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 depleted 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 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, specifically including Th and U, end up with (physically impossible) negative concentrations in the depleted mantle for both bulk crustal compositions. This provides additional, independent evidence that conventional, ε(Nd)-derived crust-mantle mass balances are based on incorrect assumptions.

Fig. 6.

Histogram of ε(Nd) values of mid-ocean ridge segment averages (Gale et al., 2013) and a new compilation of oceanic hotspot averages (Table S4, Supplementary Information). The hotspots selected for this compilation are those listed by Sleep (1990), for which published ε(Nd) data exist. 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. 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.

Fig. 7.

Partial melt models for the formation of an Early Enriched Reservoir (EER) from a primitive mantle composition. Explored melt fractions range from F = 0.08 to 0.16. X(EER) refers to the mass fraction of mantle occupied by the Early Enriched Reservoir. Solid curves are calculated using simple batch melting and partition coefficients given by Salters and Stracke (2004); dashed lines are for partition coefficients of Workman and Hart (2005). On the vertical axis, the present-day ε(Nd)-value calculated for the complementary Early Depleted Reservoir (EDR) is shown if a mass fraction of X_{EER} = 0.02 (red and yellow lines) or X_{EER} = 0.03 (blue and green lines) of EER material has been sequestered in the mantle. Thus, a relatively small amount of sequestered EER can raise the ε(Nd) value of the large, depleted residue (EDR) by several units.

Fig. 8.

Spidergrams of the trace element contents of the Early Enriched and Early Depleted Reservoirs (EER and EDR). This model is based on extracting an early-formed batch melt (melt fractions F = 0.10 and 0.12) and storing a mass fraction of X_{EER} = 0.02 or 0.03 as a hidden EER at the base of the mantle. These parameters are chosen to yield present-day ε(Nd) values close to +3.5, the minimum needed to explain the high ε(Nd) values of present-day MORB+OIB reservoirs after subsequent extraction of the continental crust from an early-depleted mantle. Partition coefficients given by SS - Salters and Stracke (2004) and WH - Workman and Hart (2005).

Fig. 9.

Isotopic evolution, shown as ε(Nd) vs. age, of EDR (Early-Depleted Reservoir, solid green line), the complementary EER (dotted green line). For clarity, the green lines show only one of the three versions of the complementary EER – EDR differentiation, namely the one corresponding to the red line shown in Fig. 8. Without further differentiation, ε(Nd) of the EDR would increase to a value of about +3.5 at the present time. In addition, we show three crust-mantle evolution trajectories, corresponding to three estimates of bulk crustal composition (yellow: Hacker et al., 2015; red: McLennan et al., 2006; blue: Rudnick & Gao, 2003). The specific case illustrated here corresponds to one of the solutions shown in Fig. 10 where the entire EDR is involved in the generation of continental crust. In addition, for clarity of illustration, we assume that all crust extraction took place as a single event 2 Ga ago. In this simplified scenario, the present-day isotopic composition of the continental crust coincidentally matches that of the EER approximately.

Fig. 10.

Final crust-mantle mass balance of the four-reservoir Earth showing the mass fraction of the residual mantle as a function of the U content of the bulk continental crust. In this mass balance the primitive mantle has been replaced by the Early-Depleted Mantle (EDR) shown in Fig. 8, which is then differentiated into continental crust and Residual Mantle. Again, the specific version of EDR chosen corresponds to the red line in Fig. 8. To explore how sensitive the results are to the precise value of $(Nb/U)_{rm}$ used for this calculation, we show three separate mass balances, one for the best value of $(Nb/U)_{rm}$ = 46 (see Tab. S2, Supplementary Information), and those for $(Nb/U)_{rm}$ = 42 and 50, which incorporate possible uncertainties somewhat beyond those for MORB data alone, and covering the majority of aberrant OIB data. For the preferred crustal U concentrations of 1.1 to 1.3 ppm and the MORB average Nb/U = 46, the mass fraction of the residual mantle, X_{rm}, ranges from 0.8 to 0.98. The corresponding residual mantle fractions for $(Nb/U)_{rm}$= 42 and 50 would be X_{rm} = 0.94 to 1.0 (>1 is physically impossible), and 0.75 to 0.9, respectively.

Fig.11.

Incompatible trace element contents of the Early-Depleted mantle and three versions of the Residual Mantle, computed for $(Nb/U)_{rm}$ = 46 and three popular versions of the composition of the bulk continental crust, RG (Rudnick & Gao, 2003) containing 1.3 ppm U which require a high value of X_{rm} = 0.97, HKB (Hacker et al., 2015) containing 1.14 ppm U, and corresponding to an intermediate value of X_{rm} = 0.9, and MTH (McLennan et al., 2006) containing 1.1 ppm U, corresponding to a relatively low value of X_{rm} = 0.8. All three crustal estimates lead to remarkably similar compositions of the residual mantle (also compare Table 1). For the heat producing elements Th and U, the discrepancies generated by the different crustal estimates do not exceed 20%. All of the newly estimated residual mantle compositions are substantially less depleted than currently used estimates given by Salters and Stracke (2004) and Workman and Hart (2005), which were based on radiogenic isotopes and the conventional three-reservoir crust-mantle differentiation model.

Fig.12.

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 20% 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.

Table 1. Composition of the residual mantle calculated by a two-stage process:

(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 permanently sequestering a mantle mass fraction of X(EER) = 0.02 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

	PriMa	C(EDR) after EER extraction	Cont. Crust (ppm)	Cont. Crust (ppm)	Cont. Crust (ppm)	**Cont. Crust normalized**	**Cont. Crust normalized**	**Cont. Crust normalized**	Residual Mantle (RM)	Residual Mantle (RM)	Residual Mantle (RM)
		SS[2] Partition Coeff.	RG[2]	MTH[2]	HKB[2]	RG[2]	MTH[2]	HKB[2]	RG[2]	MTH[2]	HKB[2]
		F(EER) = 0.1 X(EER) = 0.02						Middle = lower crust	X(RM) = 0.974	X(RM) = 0.80	X(RM) = 0.90
Rb	0.6	0.8168	49.00	37.00	40.00	81.67	61.67	66.67	0.319	0.360	0.411
Ba	6.6	0.8164	456.00	250.00	415.00	69.09	37.88	62.88	0.396	0.538	0.569
Th	0.0795	0.8186	5.60	4.20	4.29	70.44	52.83	53.96	0.390	0.428	0.472
U	0.0203	0.8193	1.30	1.10	1.14	64.04	54.19	56.16	0.430	0.419	0.464
Nb[1]	0.555	0.8215	8.00	8.00	8.10	14.41	14.41	14.59	0.738	0.720	0.731
Ta	0.037	0.8215	0.70	0.80	0.53	18.92	21.62	14.32	0.710	0.666	0.683
La	0.648	0.8229	20.00	16.00	21.00	30.86	24.69	32.41	0.638	0.644	0.664
Ce	1.675	0.8297	43.00	33.00	44.00	25.67	19.70	26.27	0.677	0.688	0.704
Pb	0.15	0.8267	11.00	8.00	11.70	73.33	53.33	78.00	0.380	0.433	0.477
Pr	0.254	0.8312	4.90	3.90	5.30	19.29	15.35	20.87	0.717	0.722	0.734
Nd	1.25	0.8353	20.00	16.00	22.00	16.00	12.80	17.60	0.742	0.746	0.755
Sm	0.406	0.8604	3.90	3.50	4.30	9.61	8.62	10.59	0.807	0.802	0.809
Zr	10.5	0.8477	132.00	100.00	138.00	12.57	9.52	13.14	0.775	0.783	0.790
Hf	0.283	0.8639	3.70	3.00	3.40	13.07	10.60	12.01	0.789	0.791	0.799
Eu	0.154	0.8675	1.10	1.10	1.20	7.14	7.14	7.79	0.829	0.820	0.826
Gd	0.544	0.8589	3.70	3.30	3.80	6.80	6.07	6.99	0.822	0.820	0.824
Tb	0.099	0.8628	0.60	0.60	0.68	6.06	6.06	6.87	0.831	0.824	0.828
Dy	0.674	0.8659	3.60	3.70	3.70	5.34	5.49	5.49	0.838	0.831	0.835
Ho	0.149	0.8765	0.77	0.78	0.79	5.17	5.23	5.30	0.850	0.844	0.847
Er	0.438	0.8844	2.10	2.20	2.10	4.79	5.02	4.79	0.860	0.853	0.857
Yb	0.441	0.8985	1.90	2.20	1.80	4.31	4.99	4.08	0.878	0.868	0.871
Lu	0.0675	0.9102	0.30	0.30	0.30	4.44	4.44	4.44	0.888	0.884	0.887
Sm/Nd						0.6004	0.6735	0.6018	1.087	1.076	1.070
Nb/U									1.716	1.717	1.577
Ce/Pb									1.781	1.590	1.477

1) The primitive mantle value of Nb = 0.658 given by McDonough and Sun (1989) has been adjusted to Nb = 0.555 ppm (see text).
2) Abbreviations: SS, RG, MTH, and HKB refer to Salters & Stracke 2004, Rudnick and Gao (2003), McLennan, Taylor and Hemming (2006), Hacker, Kelemen and Behn (2015), and Workman & Hart (2005), respectively.

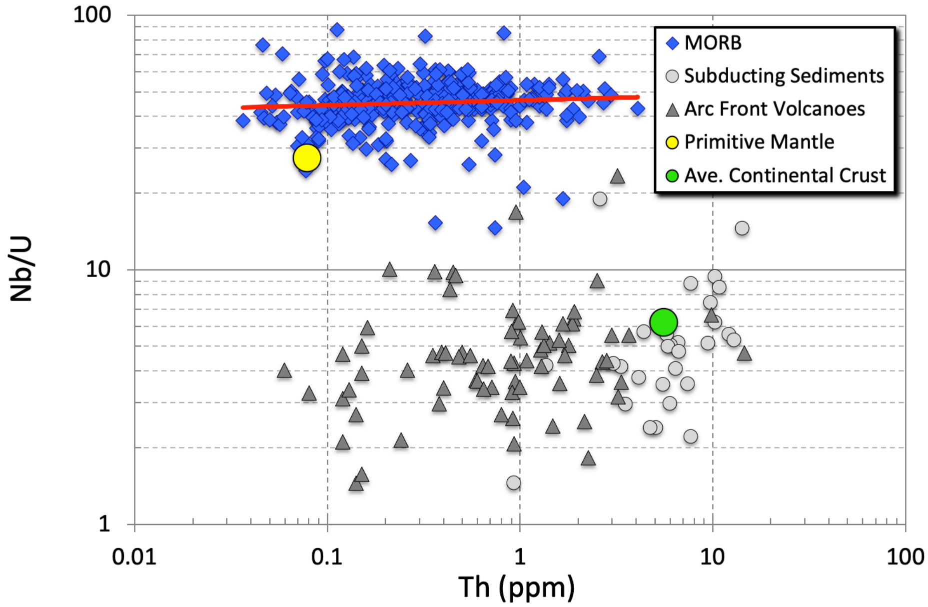

Fig. 1

1016

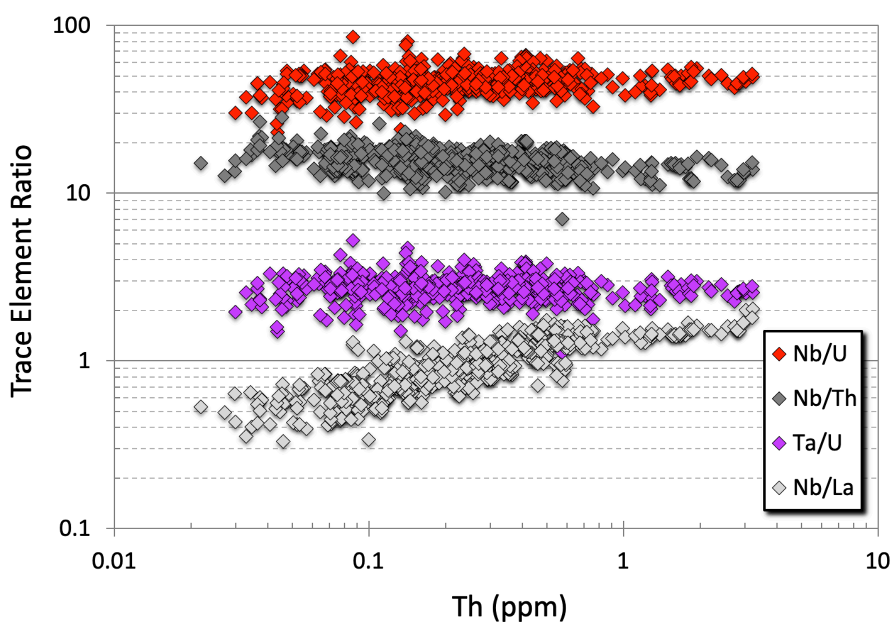

Fig. 2

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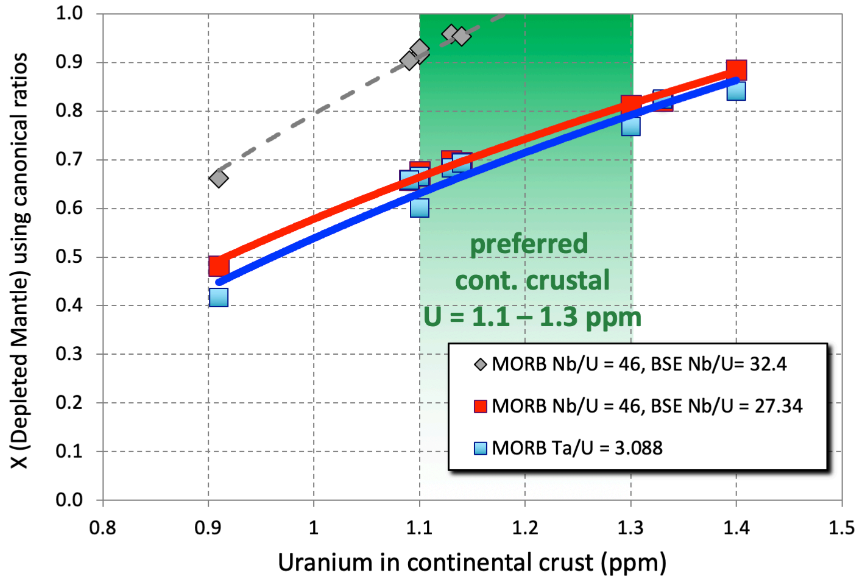

Fig. 3

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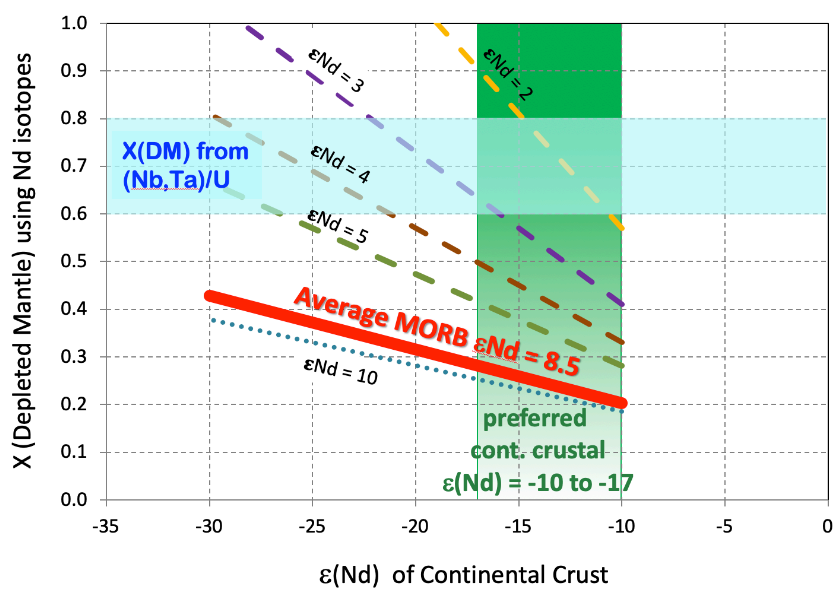

Fig. 4

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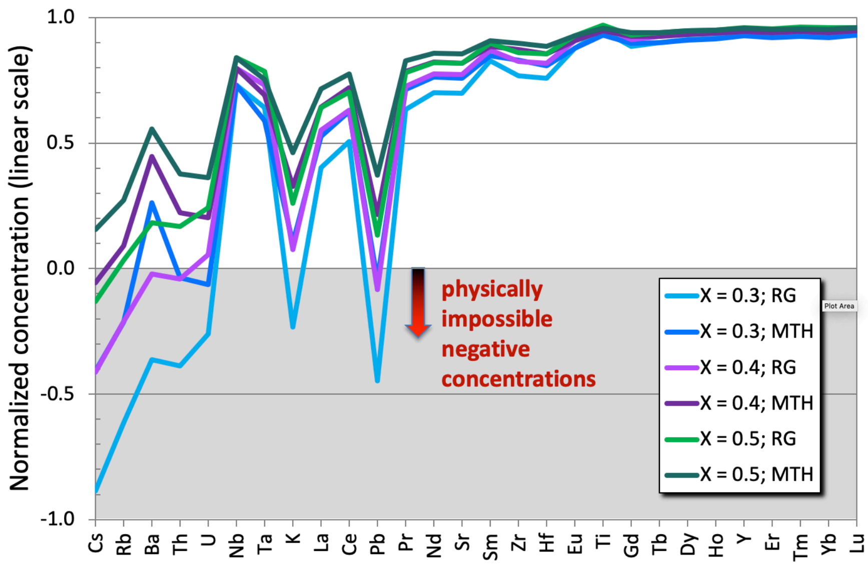

Fig. 5

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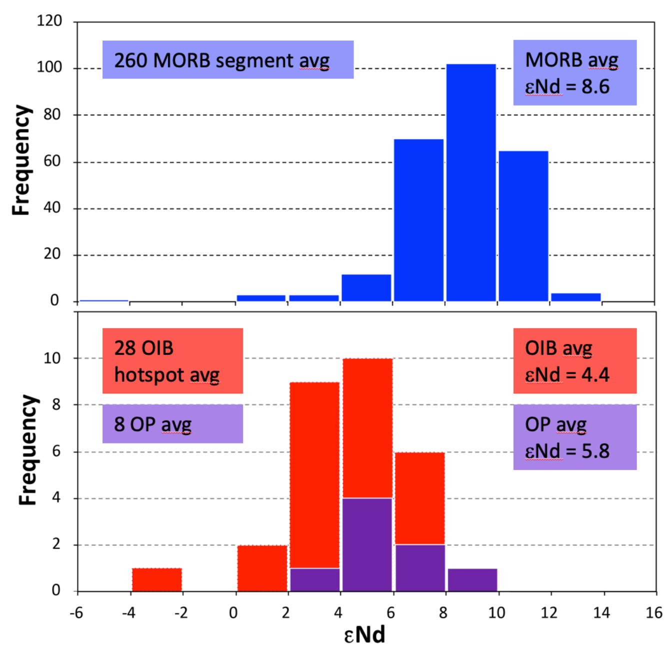

Fig. 6

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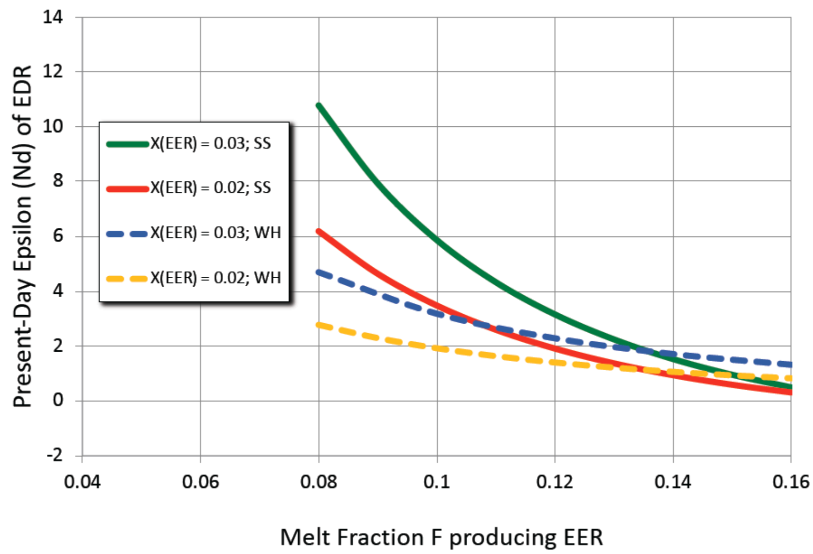

Fig. 7

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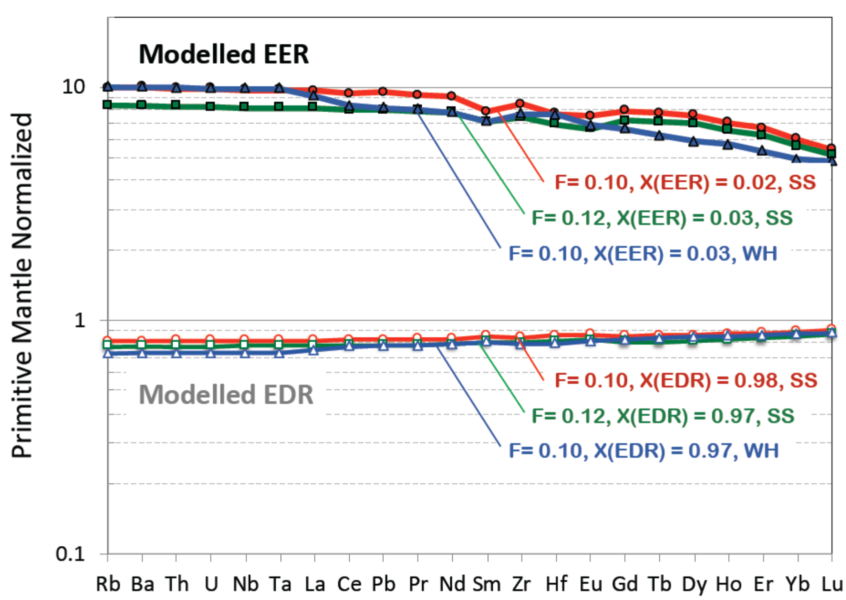

Fig. 8

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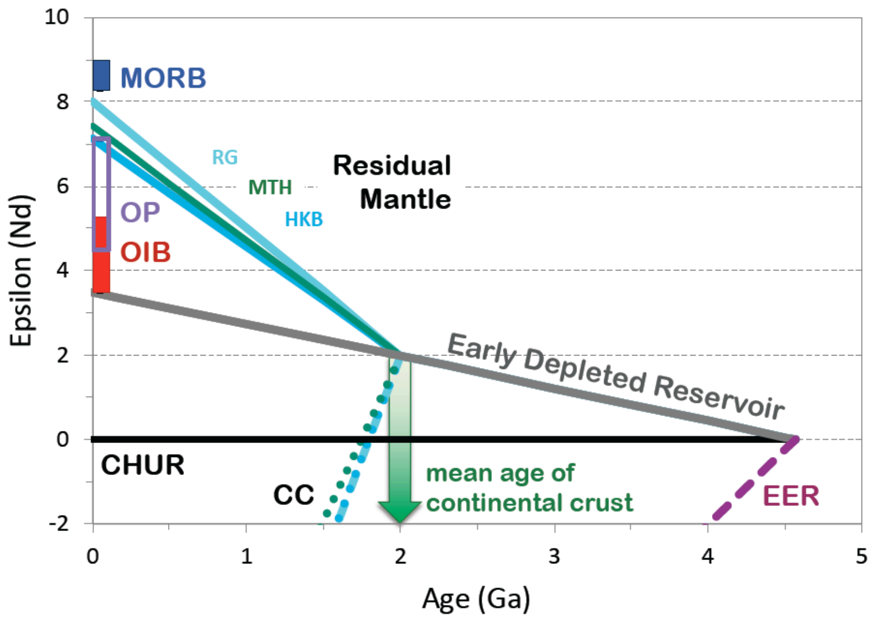

Fig. 9

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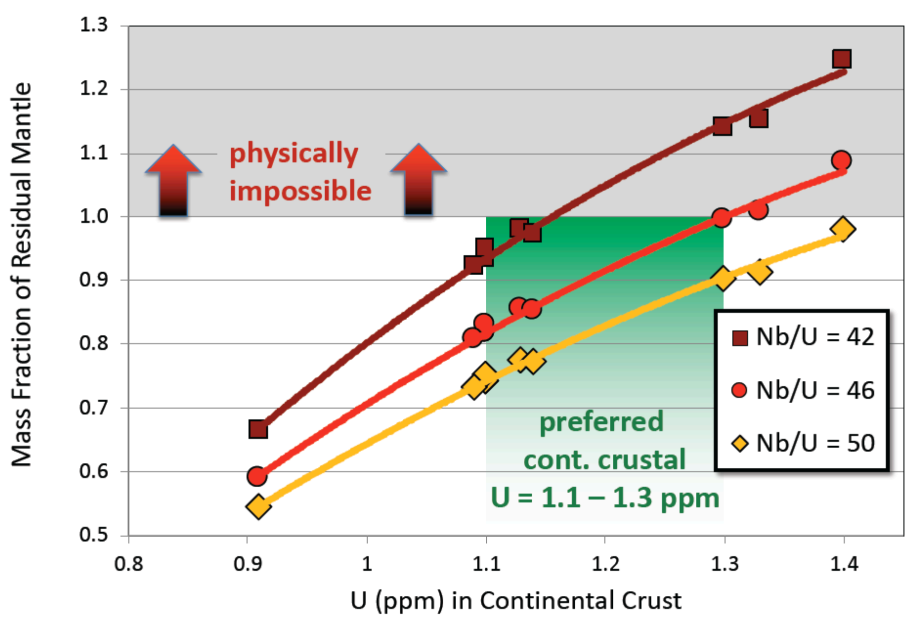

Fig. 10

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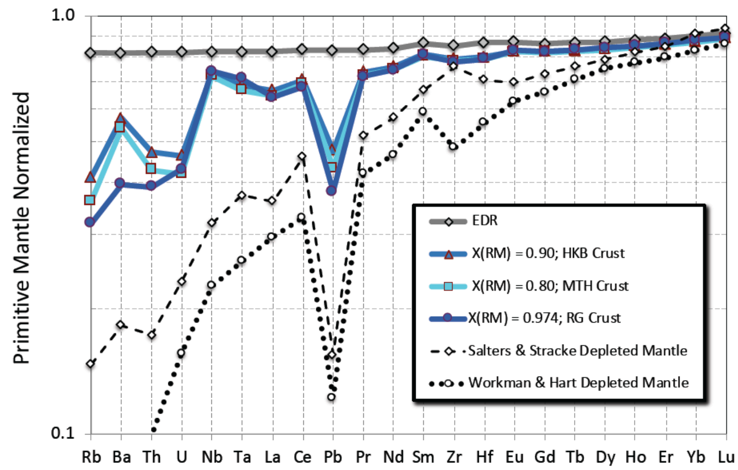
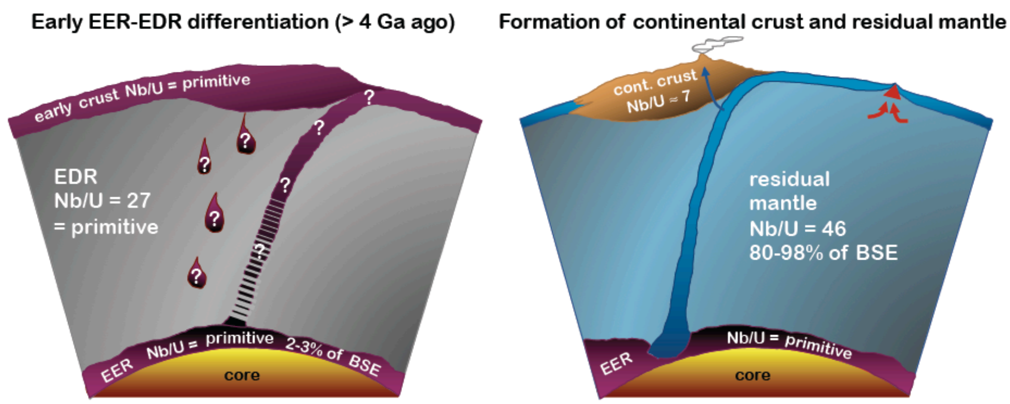


Fig. 11



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

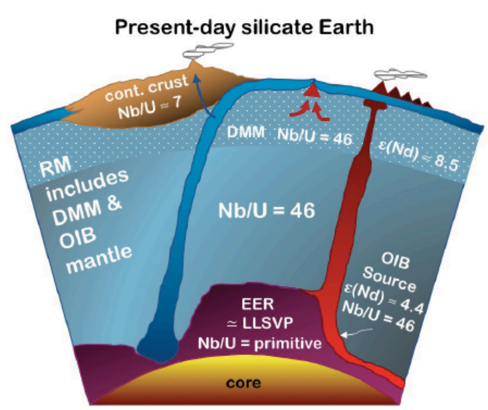


Fig. 12