Size and composition of the residual and depleted mantle reservoir

Albrecht W. Hofmann¹, Cornelia Class², and Steven L. Goldstein³

$^{1}\mathrm{MPI}$

²Lamont-Doherty Earth Observatory ³Columbia University

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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 $\varepsilon(Nd)$ 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 $\varepsilon(Nd)$ [?] 3, whereas the $\varepsilon(Nd)$ -based mass balance, using $\varepsilon(Nd) = 8.5$, 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.

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3	A	W. Hofmann, C. Class, and S. L. Goldstein
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5 6 7 8 9 10 11	Albrecht W. Hofmann (Corresponding author) Cornelia Class	Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York 10964, USA and Max Planck Institute for Chemistry, Hahn-Meitnerweg 1, 55128 Mainz, Germany <u>Albrecht.hofmann@mpic.de</u> Lamont-Doherty Earth Observatory of Columbia University,
12 13 14		Palisades, New York 10964, USA <u>class@ldeo.columbia.edu</u>
15 16 17 18 19	Steven L Goldstein	Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York 10964, USA <u>steveg@ldeo.columbia.edu</u>
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21 22	Key Points	
23	(1) Conventional assessr	nents of the size of the depleted mantle (30%), based on Nd
24	isotopes, conflict wit	h a new assessment based on Nb/U and Ta/U (> 60%).
25	(2) This conflict cannot b	e reconciled within the framework of the classical 3-reservoir
26	silicate earth (contine	ental crust, depleted mantle, primitive mantle).
27	(3) These results require	segregation of a fourth, early-enriched, small reservoir. The
28	continental crust is the	nen extracted from almost all (80 to 98%) of the mantle.
29 30 31 32 33 34 35 36	Key words:1009Geochemical1025Composition1038Mantle proce1040Radiogenic ise1065Major and tra	Modeling of the Mantle ss otope geochemistry ice element geochemistry

37 Plain Language Summary

38 The Earth's continental crust makes up only about one half of a percent of Earth's mass, but it 39 contains a large portion of its total budget of many chemical elements such as potassium and 40 phosphorus, which are critical to soil fertility, or uranium and thorium, which produce much of 41 Earth's interior heat. In making the crust, these elements have been extracted via melts and 42 volcanism from the mantle, the 3000 km thick layer of rocks beneath the crust. Therefore, part 43 of the mantle is now depleted in these important chemical elements. But what portion of the 44 mantle was involved in making the continents? In the past, geochemists thought that only its 45 uppermost third was involved, leaving the lower two-thirds of the mantle essentially 46 untouched. The measure used for this estimate is the difference between crust and mantle in 47 the accumulation of the isotope neodymium-143, the decay product of the radioactive isotope 48 samarium-147. This difference is caused by the crust and the depleted mantle having different 49 samarium/neodymium ratios. This calculation yields a depleted mantle fraction of 30%. 50 However, when we use an alternative measure for the same calculation, namely the 51 concentration ratio of niobium to uranium (Nb/U), which differs by a factor of 8 between 52 depleted mantle and continents, we find the depleted mantle fraction to be greater than 60%. 53 Both of these results cannot simultaneously be correct. We therefore need a more complex 54 Earth model, one that involves an additional "reservoir" with crust-like Sm/Nd but mantle-like 55 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 56 57 mantle, not just its uppermost layer, was involved in making our continents. A buried ancient 58 ocean crust might well explain the large density/temperature anomalies recently discovered at 59 the base of the mantle by seismologists.

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64	A.W. Hofmann ^{1,2} , C. Class ¹ , S. L. Goldstein ¹
65	
66	1. Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York 10964, USA
67	2. Max Planck Institute for Chemistry, Hahn-Meitnerweg 1, 55128 Mainz, Germany
68	
69	Abstract
70	Most previous efforts to characterize the size and composition of the upper mantle, the source
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80	exceeding 60% by mass of the total mantle (X(DM) > 0.6) with average ϵ (Nd) \leq 3, whereas the
81	ϵ (Nd)-based mass balance, using ϵ (Nd) _{MORB} = 8.5, yields a "depleted reservoir" of X(DM) \leq 0.3.
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89	(Word count: 249)

91 **1. Introduction**

92 The discovery of the trace-element depleted nature of the mantle region underlying 93 mid-ocean ridges has been one of the fundamental contributions of geochemistry to the 94 understanding of the differentiation of our planet. The first clear indication of this was probably 95 the particularly unradiogenic isotopic composition of strontium and low abundances of highly 96 incompatible elements (Gast, 1968; Hart, 1971). But the actual degree of depletion could only 97 be assessed when Nd isotopes were shown to be correlated with Sr isotopes, which allowed 98 DePaolo and Wasserburg (1976) and O'Nions et al. (1977) to tie the degree of depletion to a 99 chondritic reference frame. This had not been possible on the basis of Sr isotopes alone, because Earth's bulk Rb/Sr and ⁸⁷Sr/⁸⁶Sr ratios are not chondritic. The fact that the Sr-Nd 100 101 isotope correlation of the oceanic mantle connects to the composition of the continental crust 102 immediately led to the idea that the depletion of the MORB source is complementary to the 103 enrichment of the continental crust. O'Nions et al. (1979) and Jacobsen and Wasserburg (1979) 104 evaluated the size of the depleted mantle reservoir, using models of global crust-mantle Nd-Sr 105 isotopic evolution, and found that this reservoir constitutes only between 20 and 50% of the 106 mantle mass. This interpretation was seemingly substantiated by Hofmann (1988) who showed 107 that the complementary patterns of isotopes in MORB sources and continental crust also 108 appear to hold true for the entire suite of trace element abundances commonly used in so-109 called spidergrams.

110 At the time, the main controversial aspect concerned the importance of ocean island 111 basalts (OIBs) in the global mass-balance. Wasserburg and DePaolo (1979) suggested that OIBs 112 are derived from an undifferentiated, "primitive" reservoir in the lower mantle, and this model 113 appeared to be consistent with primordial 3 He in at least some OIBs (e.g. Kurz et al., 1982). 114 Indeed the original Nd-Sr 'mantle array' of DePaolo and Wasserburg (1976) and O'Nions et al. 115 (1977) could be explained as mixing between primitive lower mantle sources of OIB and the 116 upper mantle source of MORB. However, considering Pb isotopes, Sun and Hanson (1975) and 117 Zindler et al. (1982) showed that the OIB sources had more complex histories. Hofmann and 118 White (1980, 1982) proposed that OIB sources are dominated by recycled oceanic crust that has 119 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 Ndisotopic variations of MORBs and OIBs.

122 Subsequently, using trace elements, Hofmann et al. (1986) found that most OIBs have 123 similar or identical Nb/U (and Ce/Pb) ratios as MORBs, which are different from, and 124 complementary to, the continental crust. This further confirmed that OIBs cannot be derived 125 from a primitive mantle reservoir. The Nb/U and Ce/Pb ratios became subsequently known as 126 "canonical" ratios, because their value is essentially invariant in MORBs and most OIBs, 127 independent of the enrichment or depletion of the absolute Nb and U, or Ce and Pb, 128 concentrations respectively, over more than two orders of magnitude. Figure 1 is an updated 129 illustration of the relationship of Nb/U between global MORB (using the MORB segment 130 averages given by Gale et al., 2013), continental rocks including the continental average of 131 Rudnick and Gao (2003), arc front volcano averages of Turner et al. (2015), subducting 132 sediment averages of Plank (2014), and the primitive mantle value of McDonough and Sun 133 (1995). Thorium concentrations are used as a proxy for overall incompatible-element 134 enrichment/depletion. Figure 1 shows that, in contrast with most other trace element ratios, 135 Nb/U (as well as Ce/Pb) can efficiently discriminate between continental and intra-oceanic 136 basalt sources. Radiogenic isotope ratios are inherently less suitable for this purpose, because 137 their parent and daughter elements invariably have different partition coefficients during 138 mantle melting, and therefore parent/daughter ratios can be fractionated by both continental 139 and intra-oceanic melting processes. Hofmann et al. (1986) argued that both MORB and OIB 140 sources are residual to the continental crust, and both must have been subsequently 141 differentiated by an additional process such as the segregation and storage of oceanic crust. 142 Hofmann (1989) estimated the size of the overall mantle residue from continent extraction to 143 be greater than 50%. He did not, however, attempt to estimate the mean composition of this 144 reservoir, nor did he address the question to which extent the composition of the depleted 145 MORB-source reservoir *sensu stricto* has been affected by this additional differentiation. 146 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. 147

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

150 Subsequently, two seminal studies focused specifically on evaluating the composition of 151 the depleted MORB mantle (DMM). Salters and Stracke (2004) realized that the relationship 152 between the continental crust and the depleted MORB mantle is "not strictly complementary," 153 but did not further evaluate the potential effect of other reservoirs, such as OIB sources, on the 154 overall mass balance between the depleted MORB source (DMM) and the continental crust. 155 These authors used Hf, Nd and Sr isotopes of depleted MORB to infer the respective parent-156 daughter ratios and element concentrations of DMM. This calculation requires knowledge of 157 the temporal evolution of the depletion process, and their preferred average differentiation 158 age, 2.2 Ga, essentially coincides with what was thought to be the average age of the present-159 day continental crust. Following a somewhat different approach, Workman and Hart (2005) 160 used REE data of clinopyroxenes from oceanic peridotites to demonstrate a correlation 161 between ln(Sm) and ln(Nd). By intersecting this correlation line with the locus of Sm/Nd = 162 0.411, derived from the Nd isotopic composition of MORB and a model of continuous continent 163 extraction, they derived a depleted mantle composition significantly more depleted than the 164 one inferred by Salters and Stracke (2004). From the perspective of the present paper, it is 165 important to note that the Nd isotopic composition of MORB and the age of crust-mantle 166 differentiation play crucial roles in both of the studies just discussed. The decisive effect of the 167 extraction of the continental crust on the composition of the MORB source was also a basic 168 assumption of the global chemical differentiation model of Hofmann (1988).

169 Starting in 2005, the traditional interpretation of the terrestrial Nd-isotopic evolution 170 has been in a state of turmoil, because Boyet and Carlson (2005) demonstrated that terrestrial 171 ¹⁴²Nd/¹⁴⁴Nd ratios are higher than their chondritic counterparts by about 20 ppm. ¹⁴²Nd is the 172 daughter product of the short-lived, now extinct nuclide ¹⁴⁶Sm, and these new results appeared 173 to require that the observable terrestrial Sm/Nd ratio has increased from its initial chondritic 174 value, presumably by some kind of very early, global differentiation process that generated an 175 "early-enriched reservoir" (labeled EER) possessing lower-than-chondritic Sm/Nd, and an 176 "early-depleted reservoir" (labeled EDR) possessing higher-than-chondritic Sm/Nd. All known

177 terrestrial samples were derived from the EDR, and this implied that the enriched EER is either 178 permanently hidden deep in the Earth or lost from Earth altogether. We nevertheless mention 179 this story here, because an early-enriched reservoir had previously also been proposed by 180 Tolstikhin and Hofmann (2005) on the basis of noble gas abundances in mantle-derived basalts, 181 which demonstrate the survival of a primordial noble gas reservoir presumably located at the 182 base of the mantle. More recent research has suggested that the observed terrestrial ¹⁴²Nd/¹⁴⁴Nd excess is nucleosynthetic in origin and is therefore not caused by non-chondritic 183 ¹⁴⁷Sm/¹⁴⁴Nd or ¹⁴³Nd/¹⁴⁴Nd ratios (e.g. Burkhardt et al., 2016). If this is correct, the ¹⁴²Nd data 184 no longer require the formation of an EDR. In the course of this present paper, we will be 185 186 forced to return to the concept of an early EER-EDR differentiation, though on the basis of 187 completely different evidence.

188 In this paper, we apply a simple mass balance approach, as originally set out by Davies 189 (1981) to evaluate the proportions of the present-day mantle reservoirs by their isotopic 190 compositions. This method has the advantage of being independent of any knowledge or 191 assumptions about the timing of Earth's differentiation. It can be applied using any chemical or 192 isotopic parameter, including isotope ratios or chemical ratios that discriminate effectively 193 between the different reservoirs concerned. We initially use the canonical ratios Nb/U and 194 Ta/U, because these ratios are distinctive and well-defined for each of the main reservoirs, 195 primitive mantle, continental crust, and depleted mantle. We then compare these initial results 196 derived from the (Nb,Ta)/U parameters with the analogous calculation employing ε (Nd).

197 While the two analogous calculations should yield consistent results, in fact, they yield 198 dramatically inconsistent results, and to explain this discrepancy, we argue that the Sm/Nd 199 ratio, and consequently the ε (Nd) value, of the MORB mantle <u>sensu stricto</u> is controlled not only 200 by extraction of continental crust but also by extraction (and storage) of oceanic crust. It will be 201 seen, however, that simple inclusion of a present-day OIB source reservoir in the mass balance 202 is insufficient to resolve the overall discrepancy. Instead, an additional, hidden reservoir is 203 required, which contains primitive (Nb,Ta)/U ratios but fractionated Sm/Nd (and Lu/Hf) ratios. 204 Such an "early-enriched" reservoir (EER) could have been generated by segregating an early-205 formed mafic crust. Whether this reservoir is permanently stored in the deep mantle or ejected

206 from Earth by a collisional erosion process during late accretion is immaterial to the mass 207 balance. We assume that the complementary early-depleted reservoir (EDR) will be 208 homogenized and is subsequently differentiated into the continental crust and its mantle 209 residue, which we will call the "residual mantle" (RM), in order to distinguish it from the 210 "depleted mantle" (DM) presented initially. We will show that under such conditions the mass 211 balance calculations can yield concordant results, whereby the residual mantle occupies more 212 than 80% of the total mantle, and its incompatible trace element budget is only moderately 213 depleted. A cartoon at the end of this paper summarizes the final model.

214 We will use the following terms and symbols to describe the various terrestrial silicate 215 "reservoirs" evaluated by our mass balances:

216 CC - Bulk continental crust

217 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.
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228 2. Data assessment

229 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, highquality 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

235 versus Nb, in which the two variables employed are not independent, are inherently unsuitable 236 for a statistical assessment of the constancy of the Nb/U ratios (Sims & DePaolo, 1997). These 237 authors argued correctly that, on statistical grounds, a log Nb vs log U plot is better suited for 238 this purpose. Such log-log plots had been used extensively by Wänke et al. (1973) and also by 239 Hofmann and White (1983). A slope of 1.0 on such a plot means that the Nb/U ratio is 240 independent of the absolute concentration of either Nb or U, and under this condition the 241 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 242 243 Hofmann et al. (1986) has the advantage of displaying the uniformity of a trace element ratio in 244 a more intuitive way. Figure 2 is an example of this; it displays Nb/U, Nb/Th, Ta/U, and Nb/La as 245 functions of the absolute Th concentration in the set of about 600 MORB glasses analyzed by 246 Jenner and O'Neill (2012a). The Th concentration serves as a proxy for the relative 247 enrichment/depletion of any highly incompatible element over two orders of magnitude. This 248 shows that Nb/La, unlike Nb/U and Ta/U, should not be used as a canonical ratio, because its 249 value increases systematically by about a factor of three, as the Th value increases by a factor of 250 about 100. Using the statistically more appropriate log-log approach, Arevalo and McDonough 251 (2010) found that their global suite of MORB data yielded a log Nb vs log U slope that deviated 252 slightly but significantly from unity. Because of this, they rejected the use of Nb/U as a 253 canonical ratio for the purpose of characterizing the mantle source(s) of MORBs.

254 To address this issue we reexamine the question of which trace element ratio in oceanic 255 basalts reflects the mean composition of the residual mantle most closely and can, at the same 256 time, be used as the most effective discriminator between continental crust and residual 257 mantle. For this purpose, we use three recently published, high-quality, global data sets for 258 hundreds of MORB samples, usually fresh basalt glasses, by Arevalo and McDonough (2010), 259 Jenner and O'Neill (2012a), and Gale et al. (2013). We argue that the deviation of the slope of a 260 log-log correlation from unity need not necessarily be smaller than the statistical uncertainty of 261 this deviation, in order for such a ratio to be "canonical" in the sense that it can be used as 262 tracer of source composition. Indeed, it is exceedingly unlikely that two chemical elements 263 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).

271 For the purpose of characterizing the mean composition of a source reservoir, more 272 caution is in order if the mantle source ratios vary slightly as a function of absolute depletion or 273 enrichment, because the true mean value of the mantle may not be identical to the mean value 274 of the rocks sampled. However, the problem can still be evaluated by using more than one 275 element ratio and bracketing the results. Thus, rather than simply testing the Nb/U ratio 276 proposed thirty years ago, we determine which of a series of similarly incompatible elements is 277 closest in partitioning behavior to Nb, and we repeat this exercise for Ta. These evaluations are 278 shown in Figures S1 and S2 (Supporting Information), which illustrate examples of the log-log 279 correlation plots (Fig. S1) and the systematic relationships of the slopes of these log-log plots 280 (Figs. S2). Table S1 (Supporting Information) lists the relevant slopes and uncertainties. The 281 results for three different global MORB datasets are remarkably consistent; they demonstrate 282 that Nb/U and Ta/U bracket the ideal log-log slope of 1.00. We therefore use both of these 283 ratios to bracket our mass balance calculations. Table S2 (Supporting Information) lists the 284 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 EMtypes, 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.

291The relationships seen in Figure S2 (Supporting Information) may be translated into a292sequence of increasing compatibility of Ba < Th < Nb < U < Ta <K < La. Although none of the</td>

293 slopes conforms to the exact value of unity, the element pairs Nb – U and Ta – U come 294 remarkably close, and the "best match" for uranium would be an element with enrichment-295 depletion properties between those of Nb and Ta. Table S2 (Supporting Information) shows the 296 mean Nb/U, Ta/U, and Nb/Th ratios obtained from the three sets of MORB data. We note that 297 the three data sets agree remarkably well. The most important exception is the value of Ta/U =298 2.75 for average MORB by Jenner and O'Neill (2012a) which is significantly lower than the 299 values of 2.91 and 3.09 given by Arevalo and McDonough (2010) and by Gale et al. (2013), 300 respectively. This difference appears to be largely the result of an interlaboratory bias, because 301 Jenner and O'Neill (2012b) report a Ta value for BCR-2G that is 6.7% lower than the preferred 302 GeoReM value for this reference material. For the purpose of this paper, we will use values 303 obtained by Gale et al. (2013), because the authors of this paper took special care to obtain the 304 best representative average composition of the global mid-ocean ridge system.

305 To assess the question whether OIBs in general should be considered to be derived from 306 the same residual reservoir as MORBs, and in order to avoid the difficulties introduced by U 307 alteration, we plot the chemically more "robust" Nb/Th ratios for both global MORB and a large 308 number of OIBs and oceanic plateaus. Figure S3 shows that Nb/Th ratios of OIBs are 309 overwhelmingly part of the same population as MORBs in having Nb/Th ratios higher than 310 primitive-mantle values, analogous to Nb/U ratios. As shown in Figures 2 and S2, the Nb/Th 311 data are less reliable for quantitative evaluations of the silicate Earth mass balance because the 312 slope of the log Th vs. log Nb correlation deviates from unity more significantly than is observed 313 for log U vs log Nb or log Ta. Thus, although the Nb/Th ratio of a given basalt is likely to reflect 314 its source ratio quite closely, it is difficult to know the mean Nb/Th ratio of the bulk residual 315 mantle that incorporates both MORB and OIB sources.

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317 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, 321 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

323 (McDonough & Sun, 1995), corresponding to a Nb/Ta ratio 17.8, then thought to be the best 324 chondritic value. More recently, it has become increasingly clear that nearly all terrestrial rock 325 reservoirs have Nb/Ta ratios substantially lower than 17.8. Moreover, Münker et al. (2003) 326 redetermined the chondritic value at Nb/Ta = 19.9, using new, high-precision analyses. These 327 authors estimated the value for bulk silicate Earth to be as low as Nb/Ta = 14.0. This was in part 328 based on a rough correlation between Nb/Ta and Zr/Hf in the various rock reservoirs. Most 329 recently, Münker et al. (2017), using additional high-precision data on meteoritic silicates, 330 metals and troilites, confirmed an earlier suggestion by Wade and Wood (2001) that the 331 missing niobium may reside in Earth's core. In addition, they showed that niobium is rather 332 easily partitioned into sulfide phases at low pressures and at moderately low oxygen fugacities. 333 From these observations they inferred that much of the niobium deficiency in the silicate Earth 334 was generated in asteroidal bodies prior to Earth accretion. Consequently, the apparent 335 correlation between terrestrial Nb/Ta and Zr/Hf should no longer be used to infer the specific 336 Nb/Ta value of BSE (C. Münker, 2017, personal comm.). Currently available high-precision 337 Nb/Ta ratios are available for MORB (average 14.5 ± 1.2, Büchl et al., 2002), a variety of OIB 338 (average Nb/Ta = 15.9 ± 0.6, Pfänder et al., 2007), and several Archean greenstones (Nb/Ta = 339 15.5 ± 0.7, C. Münker et al., 2003). The similarity of these ratios in a large variety of mantle-340 derived volcanic rocks is consistent with the interpretation that the BSE Nb/Ta ratio lies 341 between 15 and 16. It will be seen below that, by using a Nb/U = 27.34, reduced from 342 McDonough and Sun's (1995) value of 32.41 and corresponding to a reduction of Nb/Ta from 343 17.78 to 15.0 for the bulk silicate Earth, we obtain concordant results when calculating the 344 amount of depleted mantle complementary to the continental crust from Nb/U and Ta/U ratios 345 in mantle and crust.

346

347 **3. Mass balance for a 3-reservoir silicate Earth**

348 **3.1. Equations and input parameters**

351 reservoir, R is a property such as an isotopic or chemical ratio, C is the concentration of the 352 chemical element in the denominator of R, and the subscripts cc, pm, and dm identify the three 353 reservoirs continental crust, primitive mantle reservoir, and depleted mantle reservoir, 354 respectively: 355 $X_{dm} + X_{pm} + X_{cc} = 1$ (1)356 357 $X_{dm} C_{dm} + X_{pm} C_{pm} + X_{cc} C_{cc} = C_{pm}$ (2) 358 359 X_{dm} C_{dm} R_{dm} + X_{pm} C_{pm} R_{pm}+ X_{cc} C_{cc} R_{cc} = C_{pm} R_{pm} (3). 360 361 The solution of these equations is: 362 363 $X_{dm} = \frac{X_{cc} C_{cc} (R_{dm} - R_{cc})}{C_{nm} (R_{dm} - R_{nm})} - X_{cc}$ 364 (4), 365 366 which is then used to evaluate the composition of the residual reservoir: 367 $C_{dm} = \frac{C_{pm} \left(X_{dm} + X_{cc} \right) - X_{cc} C_{cc}}{X_{dm}}$ 368 (5). 369 Here we specify (Nb/U)_{dm} and (Ta/U)_{dm} for R_{dm}, in order to evaluate the mass fraction of the 370 371 depleted mantle reservoir, X_{dm}, and the trace element concentrations, C_{dm}, in this reservoir. 372 Note that the version of equation (4) given by Hofmann (2003, 2014) is in error, because the 373 final term, -X_{cc.}, is missing from equation (13) in Hofmann (2003) and equation (14) in the 374 updated Hofmann (2014) version. Quantitatively, the effect of this error is very small because 375 the value of X_{cc} is so small (= 0.006).

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

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376 The input parameters for the primitive reservoir pm are taken from McDonough and 377 Sun (1995), except for the value of Nb, which we reduce from 0.658 ppm to 0.555 ppm in order 378 to take account of the Nb deficiency in the bulk silicate Earth (see discussion above). The 379 parameters for the continental crust U_{cc} , $(Nb/U)_{cc}$ and $(Ta/U)_{cc}$ are from Taylor and McLennan 380 (1985), Rudnick and Fountain (1995), (Rudnick & Gao, 2003), McLennan et al. (2006), and 381 Hacker et al. (2015); see also Table S3. We note that the estimates for the crustal abundance of 382 U in the above publications range from 0.91 to 1.4 ppm. Even higher values for the crustal U 383 abundance can be found in the literature, but will not be considered here. We further note that 384 the U value of = 0.91 ppm given by Taylor and McLennan (1985) was revised to U = 1.1 ppm by 385 McLennan et al. (2006). A minimum of U = 1.1 ppm is also found in three of the five crustal 386 models given by Hacker et al. (2015). The maximum value given by these authors is U = 1.33387 ppm, and this is nearly identical to the value of U = 1.3 ppm given by Rudnick and Gao (2003). 388 We will use a range of crustal U = 1.1 to 1.3 ppm for our estimates of the residual mantle 389 composition. Nb and Ta abundances of the bulk continental crust are less critical in the mass 390 balance calculations. McLennan et al. (2006) and Rudnick and Gao (2003) give a value of Nb = 8 391 ppm, whereas the five models of Hacker et al. (2015) yield a range of Nb = 7.4 to 8.8 ppm. In 392 contrast, the estimates of the above authors for Ta are more variable, ranging from Ta = 0.52 to 393 0.8 ppm. These variations in Nb and Ta estimates of the continental crust are the cause of only 394 minor scatter in the mass balance results seen in Fig. 3.

395 The initial assumption of a very simple, three-reservoir silicate Earth represents an 396 important simplification. Indeed, such a model harks back to the time when Earth's mantle was 397 widely thought to consist of a depleted upper and an undepleted, or "primitive" lower mantle. 398 In its simplest form, this model has largely been laid to rest by the findings of seismic 399 tomography and geochemistry. But it can nevertheless serve as a starting point in evaluations 400 of the mantle reservoir involved in forming the continental crust. It will be seen further below, 401 after our reevaluation of the analogous mass balance using Nd isotopes, that this model is in 402 fact not adequate for describing Earth's silicate interior, and this result will lead us to postulate 403 the existence of an additional, enriched, and now hidden, reservoir.

406 We initially compute a preliminary mass fraction of the depleted mantle, X_{dm}, from 407 equation (4) using the "conventional," chondrite-based BSE Nb/U ratio of 32.4 and Nb/Ta of 408 17.78 from McDonough and Sun (1995). Figure 3 shows that the depleted mantle fraction 409 calculated using this Nb/U value (gray symbols) is quite different from equivalent calculation 410 based on Ta/U (that is using values of 1.82 for the BSE (McDonough & Sun, 1995) and 3.088 for 411 average MORB (Gale et al., 2013)), which yields substantially lower depleted mantle fractions 412 (blue symbols). In addition, both calculations depend strongly on the assumed U content of the 413 continental crust, so that for crustal U abundances greater than about 1.1 ppm, the mass 414 fraction of the depleted mantle calculated from Nb/U would exceed unity, which is physically 415 impossible. As we explained in the previous section, this discrepancy between the Nb/U and 416 Ta/U-based results is almost certainly caused by the failure to take the subchondritic Nb 417 content of BSE into account. As a next step, we therefore reduce the BSE value of Nb from 418 0.658 to 0.555 ppm, corresponding to a reduction of the BSE Nb/Ta ratio to 15.0 (see previous 419 section). This reduction then leads to amounts of depleted mantle that are essentially 420 concordant with the Ta/U-based results (Fig. 3, red symbols). Overall, Figure 3 shows that, for 421 the simple three-reservoir model, the mass of the depleted mantle amounts to 60 to 80 percent 422 of the total mantle, assuming a range of crustal U values of 1.1 to 1.3 ppm as discussed above, 423 far exceeding the mass fraction of the upper mantle above 660 km of 25 to 30 %.

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

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425 **3.3. Comparison with mass balance for the 'depleted mantle' reservoir based on Nd isotopes.**

426 We now address the question why essentially all the earlier estimates yielded a much 427 smaller size of the depleted mantle reservoir of 20 to 50% (Davies, 1981; Jacobsen & 428 Wasserburg, 1979; O'Nions et al., 1979), compared to the 60 to 80% indicated by our present 429 mass balance based on canonical ratios. To evaluate this discrepancy, we now use Nd isotopes 430 with the same three-reservoir Earth model and the same mass balance (eq. (1) to (5) as above, 431 as was originally proposed by Davies, 1981). Thus, we simply replace the parameters Nb/U and 432 Ta/U by $\varepsilon(Nd)$. We reiterate that this calculation uses the implicit assumption that the depleted 433 reservoir is generated exclusively by extraction and isolation of the continental crust, thus

434 neglecting other possible differentiation mechanisms such as extraction of OIB sources. We 435 update the parameters for MORB, primitive mantle and continental crust used by Davies (1981) 436 to more current values. We use a value of $\varepsilon(Nd) = +8.5$ for MORB (the "ALL MORB" average of 437 Gale et al., 2013), and Nd concentrations of 20 ppm for the continental crust (Rudnick & Gao, 438 2003) and 1.25 ppm for the primitive mantle (McDonough & Sun, 1995). A difficulty arises when 439 choosing the $\varepsilon(Nd)$ value of the average continental crust, because the current literature gives 440 no authoritative estimates of this. Chauvel et al. (2014) use loess data to estimate the present-441 day upper continental crust at ϵ (Nd) = -10.3 ±1.2, similar to the value of ϵ (Nd) = -11.4 ±4 442 obtained by Goldstein et al. (1984) for major river systems and atmospheric dust. However, one 443 of the problems with assessing the Nd isotopic composition of the bulk crust lies in the fact that 444 this parameter depends strongly on the age of the crust. Taking loess, major rivers, and 445 atmospheric dust values as representative of the average upper crust assumes that these are 446 unbiased samples of the upper crust, which may not be the case. For example, major rivers 447 preferentially sample mountain belts and under-sample shield regions, introducing a bias 448 toward younger-than-average continent. Loess deposits sourced from mountain glaciers would 449 have a similar bias. In addition, the lower continental crust is often considered be more mafic 450 than the upper crust, or older. To our knowledge, the only attempt to evaluate the average 451 ϵ (Nd) of the lower continental crust was based on limited xenolith data (Rudnick, 1990; Rudnick) 452 & Goldstein, 1990). For example, the mean value for Archean shales from the Barberton 453 Greenstone belt is $\epsilon(Nd) = -27 \pm 4$ (Garçon et al., 2017). Thus, if the lower crust contains a 454 greater proportion of Archean rocks than does the upper crust, the estimate derived from the 455 loess-river-dusts might be significantly biased. We therefore allow a wide range of crustal $\varepsilon(Nd)$ 456 values, from -10 to -17. Figure 4 shows the results for the three-reservoir model using Nd 457 isotopes, in terms of the mass fraction of a complementary depleted mantle reservoir as a 458 function of the ε (Nd) value of the bulk continental crust. Thus, if the upper crustal value of 459 ε (Nd) = -10 applies to the bulk continental crust and the depleted mantle has an average MORB 460 composition with ϵ (Nd) = 8.5, the mass fraction of the mantle reservoir is quite small, X_{dm} = 0.2. 461 But even if the bulk crust has an ϵ (Nd) value of -17, the mass fraction of the depleted mantle

462 with $\epsilon(Nd) = +8.5$ is still only about X_{dm} = 0.3. Caro (2011, Fig. 1) arrived at essentially the same 463 conclusion on the basis of simple crust extraction models and their effects on mantle $\epsilon(Nd)$.

464 We examine this result by calculating the composition of the depleted mantle from 465 equation (5) using the mass fraction of the depleted mantle and the estimated composition of 466 the continental crust. Figure 5 shows immediately that it is not possible to extract present-day 467 continental crust of the composition given by Rudnick and Gao (2003) or McLennan et al. 468 (2006) from a mantle mass fraction as small as X = 0.3, because it would require several of the 469 most highly incompatible elements in the depleted mantle to have negative concentrations in 470 order to satisfy the mass balance with the crust, which is of course physically impossible. This 471 provides independent confirmation that the "classical," Nd-isotope based assessments of the 472 crust-mantle balance are inconsistent with current estimates of the composition of the 473 continental crust.

474 Another feature of the conventional small volume – highly depleted mantle is examined 475 in Fig. S4, which is an iteration of the partial melting model of Workman and Hart (2005) who 476 calculated a melt fraction of 6% to generate an average MORB composition from their depleted 477 mantle. By simply replacing the so-called "N-MORB" average used by Workman and Hart (2005) 478 by the modern, more representative ALLMORB average given by of Gale et al. (2013), Fig. S4 479 shows that a melt fraction of 3% would be required to generate ALLMORB from such a 480 Workman-Hart-type mantle reservoir. Such a low melt fraction is at odds with independent 481 estimates of MORB melting, which range from 8 to 20% melt fractions (Klein & Langmuir, 1987). 482

483 **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

491 invoked by Hofmann et al. (1986) to explain the observed heterogeneity in incompatible-492 element enrichment/depletion coupled with the absence of systematic differences in Nb/U in 493 MORB and OIB. In any case, the two mass balance calculations are not strictly equivalent, and it 494 might therefore be possible to resolve the differences in the two mass balances by including 495 the OIB source reservoir(s) in the mass balance calculation for ε (Nd). Unfortunately, the ε (Nd) 496 of the bulk depleted mantle (including both MORB and OIB sources) is poorly constrained. 497 Consequently, we explore this possibility by solving equation (4) for a range of potential $\varepsilon(Nd)$ 498 values that might represent the combined MORB-OIB source reservoir. Figure 4 shows that for 499 a range of crustal ε (Nd) values of -10 to -17, which includes the crustal estimates given by 500 Goldstein et al. (1984), Goldstein and Jacobsen (1988), Rudnick (1990), and Chauvel et al. 501 (2014), the bulk residual mantle would have to have an ϵ (Nd) value \leq 3.5, in order to be 502 consistent with a mass fraction of $0.8 \ge X_{dm}(Nb,Ta/U) \ge 0.6$. As will be seen below, such a low 503 ε (Nd) value is inconsistent with any plausible combination of observed ε (Nd) values of MORBs, 504 OIBs and oceanic plateaus.

505 Table S4 and Figure 6 present an informal compilation of ε (Nd) values for OIBs from 506 major hotspots and for oceanic plateaus. We selected the 28 hotspots listed by Sleep (1990) for 507 which there are adequate Nd isotope data. The hotspot data show a mean value of ϵ (Nd) = 4.37 508 \pm 2.27 (1 std deviation), corresponding to a standard error of \pm 0.43 for 28 hotspots. The Pacific 509 oceanic plateaus yield a mean value of $\varepsilon(Nd) = 5.8$. From this it seems reasonable to infer that 510 the bulk ε (Nd) value of the combined MORB-OIB mantle should be less than 8.5, the average 511 MORB value of (the average MORB value of Gale et al., 2013), but significantly greater than 4. 512 Therefore, a simple internal differentiation of the "bulk depleted" mantle into a more depleted 513 MORB reservoir and a relatively more enriched OIB-oceanic plateau source reservoir cannot 514 reconcile the mass balance based on ϵ (Nd) with the one based on (Nb,Ta)/U (compare Fig. 4: 515 ϵ (Nd) = 4, brown dashed line, only gives X_{dm} of ~33-60%). This also reinforces Campbell's (2002) 516 argument (based on partial melting considerations) that extraction of the continental crust 517 contributes only a portion of the observed change in Sm/Nd and consequently $\varepsilon(Nd)$ of the 518 residual mantle.

519 We thus conclude that these considerations constitute compelling evidence against any simple 520 three-reservoir silicate Earth model, whereby a 'depleted mantle', which may include OIB- and 521 oceanic-plateau sources as well as MORB mantle, is the sole depleted complement of the 522 continental crust. In order to reconcile the (Nb,Ta)/U-based - and the ε (Nd)-based mass 523 balances, we require an additional reservoir with a low Sm/Nd ratio but (approximately) 524 primitive Nb/U and Ta/U ratios. This reservoir is inaccessible to being sampled by melts erupted 525 at the surface. Its segregation must have increased the $\varepsilon(Nd)$ value of the observable mantle 526 without significantly affecting its Nb/U and Ta/U ratios. In other words, it must have been 527 formed prior to the segregation of the present-day continental crust. We suggest that an early-528 formed and subsequently sequestered mafic crust would meet these requirements. We will 529 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.

537 **4. The four-reservoir silicate Earth**

538 **4.1** The hidden, early-enriched reservoir (EER) and the early-depleted reservoir (EDR)

539 We now explore the consequences of the proposed hidden reservoir, the need for 540 which has been explained above. We suggest that this reservoir is generated by the formation 541 and permanent sequestration of an ancient, possibly primordial, mafic crust in a manner similar 542 to what has previously been suggested and labeled "EER" by Boyet and Carlson (2005) on 543 completely different grounds, namely the elevated, non-chondritic ¹⁴²Nd abundances of the 544 bulk silicate Earth. This mafic crust resembles oceanic crust in that its Sm/Nd and Lu/Hf ratios 545 are lower than primitive, while at the same time retaining primitive (BSE) Nb/U and Ta/U ratios. 546 Removal of such mafic material will generate an early-depleted reservoir, the EDR in the 547 nomenclature of Boyet and Carlson (2005), with elevated Sm/Nd and ε (Nd) and a moderate

548 degree of depletion of all incompatible elements. We model this using a simple batch melting 549 approach with a melt fraction of F = 0.1 and bulk partition coefficients appropriate for spinel 550 Iherzolite proposed by Salters and Stracke (2004). We then sequester a small amount of this 551 partial melt to create the EER, leaving behind a large, moderately depleted mantle reservoir, 552 labeled EDR. For the purpose of this discussion, we "aim" for an EDR having a present-day $\varepsilon(Nd)$ 553 = +3.5. This can be achieved, for example, by an EER having a mass fraction X_{EER} = 0.02 and 554 produced by batch melting with F = 0.1 (Fig. 7). Alternatively, such an EDR can also be 555 generated by a moderately higher melt fraction of F = 0.12 for generating the EER, and a 556 corresponding increase in the amount of sequestered EER ($X_{EER} = 0.03$). Using the partition 557 coefficients suggested by Workman and Hart (2005), a similar result can be achieved by 558 choosing the combination of F = 0.10 and X_{EER} = 0.03. We then calculate the complete trace 559 element composition of this EDR. Figure 8 shows that in such an early depleted mantle, the 560 concentrations of the most highly incompatible elements are reduced to values ranging 561 between roughly 70 and 80% of the original BSE values. We note that this degree of depletion is 562 considerably more moderate than a reduction of U and Th by fully 50% as a result of "collisional 563 erosion suggested by O'Neill and Palme (2008).

564 Figure 9 evaluates subsequent Nd-evolution models for one of the above EDR models, 565 corresponding to partition coefficients of Salters and Stracke (2004) and values of F = 0.1 and X_{EER} = 0.02. This raises the ¹⁴⁷Sm/¹⁴⁴Nd ratio of the complementary EDR from its chondritic 566 567 value, 0.1960 (Bouvier, 2008), to a value of 0.2019, and generates a present-day ε (Nd) = 3.49 of 568 the EDR. This is the new base line of the Nd isotope evolution, from which the continental crust 569 is differentiated. The subsequent extraction of the present-day continental crust is shown, for 570 simplicity, as a single event at 2.0 Ga intended to broadly represent the mean age of the 571 present-day continental crust (Figure 9). The value of 2.0 Ga compares with mean age 572 estimates of 1.82 Ga by Chauvel et al. (2014), 2.0 Ga by Goldstein et al. (1984). and 2.1 Ga by 573 (e.g. Goldstein & Jacobsen, 1988), We use the estimates of the bulk Sm and Nd concentrations 574 of the continental crust of three different studies (Hacker et al., 2015; McLennan et al., 2006; 575 Rudnick & Gao, 2003) to represent the range of likely isotopic compositions of the present-day 576 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.

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580 **4.2. Mass balance of the four-reservoir Earth**

581 We now use the proposed EDR as a new starting composition to recalculate the mass 582 balance of a new three-reservoir system encompassing EDR, continental crust, and residual 583 mantle (RM). Overall, this actually represents a four-reservoir system in which one reservoir, 584 the EER, has been estimated by an *a priori* forward model, designed to reconcile the two 585 independent mass balances for the remaining three reservoirs (i.e. those based on Nd isotopes 586 and on (Nb,Ta)/U ratios). Figure 10 shows that size of the residual reservoir, X_{RM} (=mantle 587 residue after extraction of present-day continental crust from the EDR), occupies between 80 588 and nearly 100% of the mantle, depending on the specific U content of the crust within our 589 preferred range of U = 1.1 and 1.3 ppm, using the MORB value of Nb/U = 46 for the combined 590 MORB-OIB source to represent the composition of the entire residual mantle. This range thus 591 includes possible cases where the entire silicate Earth is "residual" except for the 2 to 3% 592 required for the EER and the 0.006% taken up by the continental crust, as well as cases where 593 up to nearly 20% of the silicate Earth may still have its original EDR composition. Figure 10 also 594 shows the respective results for cases where the bulk residual Nb/U might be different from the 595 MORB value of 46. This range of Nb/U values reflects an approximate uncertainty introduced by 596 the inclusion of the OIB sources. The results for Nb/U = 42 and 50 shown in Fig. 10 demonstrate 597 that the residual mantle reservoir still takes up more than 70% of the total mantle even if Nb/U 598 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

606 estimates given by previous workers (Salters & Stracke, 2004; Workman & Hart, 2005), shown 607 here for comparison. Aside from this lower degree of depletion, the magnitude of the negative 608 Pb anomaly is more variable and less extreme than those given in previous estimates (Salters & 609 Stracke, 2004; Workman & Hart, 2005). This is most likely the result of the greater uncertainty 610 in the Pb concentration in the continental crust relative to those of the REE abundances in the 611 various estimates. The more important point, however, is that all of the U and Th abundances 612 of the new are residual mantle estimates are three to four times higher than those given by 613 Workman and Hart (2005) and about two to three times higher than those given by Salters and 614 Stracke (2004). In particular, the abundances of Th and U are roughly 40 to 50% of their 615 respective primitive-mantle values, rather than 10 to 20% as previously estimated. The earlier, 616 much more extreme depletions were direct results of the assumption that the depleted MORB 617 source is the sole residue of the continental crust.

618

619 **5. Summary and concluding discussion**

620 We have reevaluated the global crust-mantle differentiation of the traditional three-621 reservoir silicate Earth consisting of continental crust, depleted mantle, and primitive mantle 622 reservoirs. The mass of the depleted reservoir exceeds 60% of the total mantle if we use Nb/U 623 and Ta/U ratios as discriminants between continental crust and depleted mantle. The 624 analogous result based on Nd isotopes (instead of (Nb,Ta/U)) yields a depleted reservoir mass 625 of only 30%, if its ε (Nd) value is 8.5 (the current best MORB average), and still less than 50% if 626 its ε (Nd) is as low as +4 (close to the OIB average). Thus, the three-reservoir model is unable to 627 simultaneously account for both parameters used as measures of crust-mantle differentiation. 628 The conflicting mass balance constraints can be reconciled with a four-reservoir Earth 629 model (Fig. 12) including an additional, early-enriched mantle reservoir (EER) and its 630 complement, the early-depleted reservoir (EDR – Fig.12a). We assume that these reservoirs 631 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 632 633 in incompatible elements, and it serves as a source for the continental crust (Fig. 12b). Nb/U 634 and Ta/U ratios are fractionated during continent formation. The residue of continental crust

635 formation is the "residual mantle", which occupies at least 80% of the total mantle, and it may 636 occupy all of it, except for the EER itself. This means that only 0 to 20% of the original EDR 637 survives to the present day. The trace element composition of the residual mantle is not nearly 638 as depleted as currently used estimates of "depleted"-mantle compositions (Fig. 11). The 639 residual mantle reservoir has been further differentiated into more depleted MORB mantle 640 (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 641 642 discussed below, the EER and possible remnants of the EDR might reside in the present-day LLSVP. 643

644 The EER is likely to have originated as an early mafic crust characterized by a lower-645 than-primitive Sm/Nd ratio but primitive (Nb,Ta)/U ratios. It might thus be quite similar to that 646 postulated earlier by Boyet and Carlson (2005) and Carlson and Boyet (2008) on the basis of ¹⁴²Nd isotopes, and by Tolstikhin and Hofmann (2005) on the basis of xenon isotopes; however, 647 648 our present argument for its existence does not rest on the evidence of short-lived nuclides. 649 Alternatively, our results are consistent with models of complete removal of an early mafic 650 crust, such as has been proposed by O'Neill and Palme (2008) in their model of collisional 651 erosion.

652 The mass balance as discussed here addresses only the presently existing mantle and 653 crustal reservoirs; it does not address the question of what happened to potentially large 654 amounts of early Archean continental crust, now vanished but widely thought to have existed 655 at one time. In contrast with the EM-type OIBs, where the recycled continental materials are 656 clearly recognizable by their correlated Nb/U and Ce/Pb and isotopic signatures, (e.g. Jackson et 657 al., 2007), any vanished early Archean continental crust cannot be identified in this manner, 658 and we must assume that this material has been sufficiently well rehomogenized with the 659 residual mantle, so that it has become an indistinguishable part of it. In any case, while the fate 660 of the early Archean crust is important for the understanding of crustal evolution, it is of no 661 particular consequence for the narrower purpose of mass balance evaluations of the present-662 day crust and its mantle residue.

663 Finally, we briefly revisit the possibility that the Early Enriched Reservoir is located 664 within the LLSVPs (Large Low Shearwave Velocity Provinces), as shown in our cartoon of mantle 665 evolution (Figure 12). These lower-mantle provinces have been recognized and delineated 666 relatively recently (e.g. Dziewonski et al., 2010; Garnero & McNamara, 2008), and their total 667 mass has been difficult to evaluate, with estimates ranging from 2% (Burke et al., 2008) to 9% 668 of the silicate earth (Cottaar & Lekic, 2016). Their ages are essentially unknown, but might well 669 approach the age of the Earth. Most workers agree that the LLSVPs are compositionally 670 different from the surrounding and overlying mantle rocks. Thus, it is possible that an early-671 enriched reservoir, as well as an essentially primitive reservoir, have survived in these LLSVPs 672 (e.g.Lau et al., 2017). For example, Ballmer et al. (2016) have proposed a geodynamic model 673 whereby the lower portion of the LLSVP is primitive, whereas the upper portion consists of 674 recycled basaltic crust. Although our simplified three-reservoir treatment does not specifically 675 address these issues, it is certainly consistent with the existence of LLSVPs possessing a 676 relatively complex internal structure and compositional contrasts. Recent noble gas analyses of 677 Xe, Ne and He in Iceland basalts compared with MORB also demand the formation and survival 678 of an EER to explain the observed isotopic distinctions (e.g. Mukhopadhyay, 2012). We suggest 679 that the noble gases contained in the EER leak into the mantle-plume sources by diffusion. This 680 is consistent with dynamic Earth models in which plumes are derived predominantly from the 681 boundary layer above the LLSVPs, because the refractory elements in mantle plumes are 682 dominated by recycled material that is significantly younger and possesses elevated (Nb,Ta)/U 683 ratios caused by the extraction of continental crust.

684 In conclusion, previously published $\varepsilon(Nd)$ -based estimates of the size and composition 685 of the residual, depleted mantle are systematically in error, because they assume the 686 continental crust to be the sole complement of the MORB-source mantle. The actual 687 continental-crust residue includes both MORB and OIB sources. We have shown that no simple 688 3-reservoir mantle model consisting of a primitive reservoir, a continental crust, and a depleted 689 mantle reservoir is simultaneously consistent with the mass-balance constraints imposed by the 690 observed Nd isotopic compositions and the (Nb,Ta/U) ratios of mantle and crust. Specifically, 691 the $\varepsilon(Nd)$ -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.

694 The internal inconsistencies of the three-reservoir models can be resolved by 695 introducing a fourth reservoir. Such a reservoir may have been formed by the permanent 696 segregation of an early mafic crust (= early enriched reservoir, EER). This would cause an 697 increased Sm/Nd ratio in the remaining mantle, here called "EDR" (= Early Depleted Reservoir), 698 while Nb/U and Ta/U ratios of both EER and EDR would retain their BSE values, because this 699 mafic crust was not "continental" in nature. Our recalculation of the subsequent crust-mantle 700 differentiation yields a mass of the residual reservoir exceeding 80%, and possibly close to 701 100%. It is much less depleted in highly incompatible elements, in particular the heat producers 702 Th and U, than given by traditional, isotope-based estimates. Thus the heat production of the 703 present-day residual mantle comprising both MORB and OIB sources is about 40-50% of the 704 bulk silicate value, rather than 10 - 20% as estimated by traditional, isotope-based models. The 705 distribution of these heat sources between the relatively more incompatible element enriched 706 OIB sources and the more depleted MORB sources should be a subject of future investigations. 707

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709 References

- 710
- Arevalo Jr, R., & McDonough, W. F. (2010). Chemical variations and regional diversity observed
 in MORB. *Chemical Geology*, 271(1-2), 70-85.
- Ballmer, M. D., Schumacher, L., Lekic, V., Thomas, C., & Ito, G. (2016). Compositional layering
 within the large low shear-wave velocity provinces in the lower mantle. *Geochemistry*, *Geophysics, Geosystems*, 17(12), 5056-5077.
- Boyet, M., & Carlson, R. W. (2005). 142Nd Evidence for Early (>4.53 Ga) Global Differentiation
 of the Silicate Earth. *Science*, *309*(5734), 576-581.
- Büchl, A., Münker, C., Mezger, K., & Hofmann, A. W. (2002). Hihg-precision Nb/Ta and Ze/Hf
 ratios in global MORB. *Geochimica et Cosmochimica Acta, 66 Suppl.A*, A 108.
- Burke, K., Steinberger, B., Torsvik, T. H., & Smethurst, M. A. (2008). Plume Generation Zones at
 the margins of Large Low Shear Velocity Provinces on the core-mantle boundary. *Earth and Planetary Science Letters, 265*(1-2), 49-60.
- Burkhardt, C., Borg, L. E., Brennecka, G. A., Shollenberger, Q. R., Dauphas, N., & Kleine, T.
 (2016). A nucleosynthetic origin for the Earth's anomalous 142Nd composition. *Nature*, *537*(7620), 394-398. Letter
- Campbell, I. H. (2002). Implications of Nb/U, Th/U and Sm/Nd in plume magmas for the
 relationship between continental and oceanic crust formation and the development of
 the depleted mantle. *Geochim. Cosmochim. Acta, 66*, 1651-1661.
- Carlson, R. W., & Boyet, M. (2008). Composition of Earth's interior: The importance of early
 events. *Phil. Trans. R. Soc. Lond. A, 366*, 4077-4103.
- 731 Caro, G. (2011). Early silicate earth differentiation. Annu. Rev. Earth Planet. Sci., 39, 31-58.
- Chauvel, C., Garcon, M., Bureau, S., Besnault, A., Jahn, B.-m., & Ding, Z. (2014). Constraints from
 loess on the Hf-Nd isotopic composition of the upper continental crust. *Earth and Planetary Science Letters, 388*(0), 48-58.
- Christensen, U. R., & Hofmann, A. W. (1994). Segregation of subducted oceanic crust in the
 convecting mantle. *J. Geophys. Res., 99*, 19,867-819,884.
- Cottaar, S., & Lekic, V. (2016). Morphology of seismically slow lower-mantle structures.
 Geophysical Journal International, 207(2), 1122-1136.
- Davies, G. F. (1981). Earth's neodymium budget and structure and evolution of the mantle.
 Nature, 290, 208-213.
- DePaolo, D. J., & Wasserburg, G. J. (1976). Inferences about Magma Sources and Mantle
 Structure from Variations of 143Nd/144Nd. *Geophys. Res. Lett., 3*(12), 743-746.
- 743 Dziewonski, A. M., Lekic, V., & Romanowicz, B. A. (2010). Mantle Anchor Structure: An
 744 argument for bottom up tectonics. *Earth and Planetary Science Letters, 299*(1-2), 69-79.
- Gale, A., Dalton, C. A., Langmuir, C. H., Su, Y., & Schilling, J.-G. (2013). The mean composition of
 ocean ridge basalts. *Geochemistry, Geophysics, Geosystems, 14*, 489-518.
- Garçon, M., Carlson, R. W., Shirey, S. B., Arndt, N. T., Horan, M. F., & Mock, T. D. (2017). Erosion
 of Archean continents: The Sm-Nd and Lu-Hf isotopic record of Barberton sedimentary
 rocks. *Geochimica et Cosmochimica Acta, 206* (Supplement C), 216-235.
- Garnero, E. J., & McNamara, A. K. (2008). Structure and Dynamics of Earth's Lower Mantle.
 Science, *320*(5876), 626-628.

- Gast, P. W. (1968). Trace element fractionation and the origin of tholeiitic and alkaline magma
 types. *Geochim. Cosmochim. Acta, 32*, 1057-1086.
- Goldstein, & Jacobsen, S. B. (1988). Nd and Sr isotopic systematics of river water suspended
 material: implications for crustal evolution. *Earth and Planetary Science Letters*, 87(3),
 249-265.
- Goldstein, S. L., O'Nions, R. K., & Hamilton, P. J. (1984). A Sm-Nd isotopic study of atmospheric
 dusts and particulates from major river systems. *Earth Planet. Sci. Lett., 70*, 221-236.
- Hacker, B. R., Kelemen, P. B., & Behn, M. D. (2015). Continental lower crust. *Annu. Rev. Earth Planet. Sci., 43*, 167-205.
- Hart, S. R. (1971). K, Rb, Cs, Sr, Ba contents and Sr isotope ratios of ocean floor basalts. *Philos. Trans. R. Soc. London. Ser. A., 268*, 573-587.
- Hofmann, A. W. (1988). Chemical differentiation of the Earth: the relationship between mantle,
 continental crust, and oceanic crust. *Earth Planet. Sci. Lett.*, *90*, 297-314.
- Hofmann, A. W. (1989). Geochemistry and models of mantle circulation. *Phil. Trans. R. Soc. Lond. A, 328*, 425-439.
- Hofmann, A. W. (2003). Sampling mantle heterogeneity through oceanic basalts: Isotopes and
 trace elements. In R. W. Carlson (Ed.), *Vol. 2 The Mantle and Core* (Vol. 2, pp. 61-101).
 Oxford: Elsevier-Pergamon.
- Hofmann, A. W. (2014). 3.3 Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes
 and Trace Elements. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on Geochemistry (Second Edition)* (pp. 67-101). Oxford: Elsevier.
- Hofmann, A. W., Jochum, K.-P., Seufert, M., & White, W. M. (1986). Nb and Pb in oceanic
 basalts: new constraints on mantle evolution. *Earth Planet. Sci. Lett.*, *79*, 33-45.
- Hofmann, A. W., & White, W. M. (1980). The role of subducted oceanic crust in mantle
 evolution. *Carnegie Inst. Wash. Year Book, 79*, 477-483.
- Hofmann, A. W., & White, W. M. (1982). Mantle plumes from ancient oceanic crust. *Earth Planet. Sci. Lett.*, *57*, 421-436.
- Hofmann, A. W., & White, W. M. (1983). Ba, Rb, and Cs in the Earth's mantle. *Z. Naturforsch.*,
 38, 256-266.
- Jackson, M. G., Hart, S. R., Koppers, A. A. P., Staudigel, H., Konter, J., Blusztajn, J., et al. (2007).
 The return of subducted continental crust in Samoan lavas. *Nature*, 448(7154), 684-687.
- Jacobsen, S. B., & Wasserburg, G. J. (1979). The mean age of mantle and crustal reservoirs. J.
 Geophys. Res., 84, 7411-7427.
- Jenner, F. E., & O'Neill, H. S. C. (2012a). Analysis of 60 elements in 616 ocean floor basaltic
 glasses. *Geochem. Geophys. Geosyst.*, 13, Q02005.
- Jenner, F. E., & O'Neill, H. S. C. (2012b). Major and trace analysis of basaltic glasses by laser ablation ICP-MS. *Geochem. Geophys. Geosyst., 13*, Q03003.
- Klein, E. M., & Langmuir, C. H. (1987). Global correlations of ocean ridge basalt chemistry with
 axial depth and crustal thickness. *J. Geophys. Res., 92*, 8089-8115.
- Kurz, M. D., Jenkins, W. J., & Hart, S. R. (1982). Helium isotopic systematics of oceanic islands:
 implications for mantle heterogeneity. *Nature*, 297, 43-47.
- Lau, H. C. P., Mitrovica, J. X., Davis, J. L., Tromp, J., Yang, H.-Y., & Al-Attar, D. (2017). Tidal
 tomography constrains Earth's deep-mantle buoyancy. *Nature*, 551, 321. Article

795 McDonough, W. F., & Sun, S.-S. (1995). The composition of the Earth. Chem. Geol., 120, 223-796 253. 797 McLennan, S. M., Taylor, S. R., & Hemming, S. R. (2006). Composition, differentiation, and 798 evolution of continental crust: Constraints from sedimentary rocks and heat flow. In M. 799 Brown & T. Rushmer (Eds.), Evolution and Differentiation of the Continental Crust (pp. 800 92-134): Cambridge Univ. Press. 801 Mukhopadhyay, S. (2012). Early differentiation and volatile accretion recorded in deep-mantle 802 neon and xenon. Nature, 486(7401), 101-104. 10.1038/nature11141 803 Münker, C., Fonseca, R. O. C., & Schulz, T. (2017). Silicate Earth's missing niobium may have 804 been sequestered into asteroidal cores. Nature Geoscience, 10, 822. Article 805 Münker, C., Pfänder, J. A., Weyer, S., Büchl, A., Kleine, T., & Mezger, K. (2003). Evolution of 806 planetary cores and the earth-moon system from Nb/Ta systematics. Science, 807 301(5629), 84-87. 808 O'Neill, H. S. C., & Palme, H. (2008). Collisional erosion and the non-chondritic composition of 809 the terrestrial planets. Phil. Trans. R. Soc. A, 366, 4205-4238. O'Nions, R. K., Evensen, N. M., & Hamilton, P. J. (1977). Variations in ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr 810 811 ratios in oceanic basalts. Earth Planet. Sci. Lett., 34, 13-22. 812 O'Nions, R. K., Evensen, N. M., & Hamilton, P. J. (1979). Geochemical modeling of mantle 813 differentiation and crustal growth. J. Geophys. Res., 84, 6091-6101. 814 Pfänder, J. A., Münker, C., Stracke, A., & Mezger, K. (2007). Nb/Ta and Zr/Hf in ocean island 815 basalts -- Implications for crust-mantle differentiation and the fate of Niobium. Earth 816 and Planetary Science Letters, 254(1-2), 158-172. 817 Plank, T. (2014). The Chemical Composition of Subducting Sediments. In H. D. Holland & K. K. 818 Turekian (Eds.), Treatise on Geochemistry (Second Edition) (Vol. 4.17, pp. 607-629). 819 Oxford: Elsevier. 820 Rudnick, R. L. (1990). Nd and Sr isotopic compositions of lower-crustal xenoliths from north 821 Queensland, Australia: Implications for Nd model ages and crustal growth processes. 822 *Chem. Geol., 83*(3/4), 195-208. Rudnick, R. L., & Fountain, D. M. (1995). Nature and composition of the continental crust: a 823 824 lower crustal perspective. *Rev. Geophysics*, 33, 267-309. 825 Rudnick, R. L., & Gao, S. (2003). Composition of the continental crust. In R. L. Rudnick (Ed.), 826 Treatise on Geochemistry (Vol. 3 The Crust, pp. 1-64): Elsevier. 827 Rudnick, R. L., & Goldstein, S. L. (1990). The Pb isotopic compositions of lower crustal xenoliths 828 and the evolution of lower crustal Pb. Earth Planet. Sci. Lett., 98, 192-207. 829 Salters, V. J. M., & Stracke, A. (2004). Composition of the depleted mantle. *Geochem. Geophys.* 830 *Geosystems*, *5*, doi:10.1029/2003GC000597. 831 Sims, K. W. W., & DePaolo, D. J. (1997). Inferences about mantle magma sources from 832 incompatible element concentration ratios in oceanic basalts. Geochim. Cosmochim. 833 Acta, 61, 765-784. 834 Sleep, N. H. (1990). Hotspots and mantle plumes: Some phenomenology. J. Geophys. Res., 95, 835 6715-6736. 836 Sun, S. S., & Hanson, G. N. (1975). Evolution of the mantle: Geochemical evidence from alkali 837 basalt. Geology, 3, 297-302.

- Taylor, S. R., & McLennan, S. M. (1985). *The continental crust: its composition and evolution*.
 Oxford: Blackwell Scientific Publications.
- Tolstikhin, I. N., & Hofmann, A. W. (2005). Early Crust on top of the Earth's core. *Phys. Earth Planet. Interiors, 148,* 109-130.
- Turner, S. J., & Langmuir, C. H. (2015). The global chemical systematics of arc front
 stratovolcanoes: Evaluating the role of crustal processes. *Earth and Planetary Science Letters, 422*(0), 182-193.
- Wade, J., & Wood, B. J. (2001). The Earth's 'missing' niobium may be in the core. *Nature, 409*,
 75-78.
- 847 Wänke, H., Baddenhausen, H., Dreybus, G., Jagoutz, E., Kruse, H., & Palme, H. (1973).
- Multielement analyses of Apollo 15, 16, and 17 samples and the bulk composition of the
 moon. Proceedings of the Fourth Lunar Science Conference (Suppl 4, Geochim.
 Cosmochim. Acta), 2, 1461-1481.
- Wasserburg, G. J., & DePaolo, D. J. (1979). Models of Earth Structure Inferred from Neodymium
 and Strontium Isotopic Abundances. *Proc. Natl. Acad. Sci. U. S. A., 76*(8), 3594-3598.
- Workman, R. K., & Hart, S. R. (2005). Major and trace element composition of the depleted
 MORB mantle (DMM). *Earth and Planetary Science Letters*, 231(1-2), 53-72.
- Zindler, A., Jagoutz, E., & Goldstein, S. L. (1982). Nd, Sr, and Pb isotopic systematics of a threecomponent mantle: a new perspective. *Nature, 298*, 519-523.
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858	Figure Captions
859	
860	Fig. 1.
861	Nb/U vs. Th for mid-ocean ridge basalts (MORB), using MOR segment averages of Gale et al.
862	(2013), average continental crust (Rudnick & Gao, 2003), primitive mantle (McDonough & Sun,
863	1995), average values for arc front volcanoes (Turner & Langmuir, 2015) and for subducting
864	sediments (Plank, 2014). Thorium concentrations are used as a proxy for overall incompatible-
865	element enrichment/depletion. The primitive mantle (McDonough & Sun, 1995) is shown with
866	a reduced Nb value of 0.555 ppm, instead of Nb = 0.658 recommended by McDonough and Sun
867	(1995), to account for the loss of Nb from the bulk silicate Earth compared to chondrites (see
868	section on reassessment of the Nb-Ta-Th-U relationships in oceanic basalts).
869	
870	Fig. 2
871	Nb/U, Ta/U, Nb/Th, and Nb/La versus Th concentrations in about 600 MORB glasses. Data from
872	Jenner and O'Neill (2012a). This illustrates the essential property of "canonical" trace element
873	ratios: They remain essentially constant and independent of source/melt depletion or
874	enrichment in mantle-derived basalts. Nb/U and Ta/U meet this requirement nearly perfectly,
875	whereas Nb/Th decreases slightly as a function of increasing Th. All three of these ratios are
876	useful tracers of source composition. In contrast, Nb/La increases by about a factor of three as
877	Th increases by two orders of magnitude, and it is unsuitable as a "canonical" ratio.
878	
879	Fig. 3.
880	Mass fraction of depleted mantle, X_{dm} , based on canonical ratios in a three-reservoir Earth
881	model. X_{dm} is calculated from equ. (5) and a MORB average of Nb/U = 46 given by Gale et al.
882	(2013) and Jenner and O'Neill (2012a), as well as Ta/U = 3.088 from Gale et al. (2013) as the R_{dm}
883	parameters. The resulting value of X_{dm} depends significantly on the bulk uranium content
884	assumed for the continental crust, U_{cc} . We use a variety of published crustal uranium estimates
885	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.

- 894
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- 896 Fig. 4.

897 Mass fraction of depleted mantle, X_{dm}, based on Nd isotope ratios in a three reservoir Earth 898 model. Mass balance results are shown for a range of possible ε (Nd) values of mantle and crust. 899 The range of acceptable crustal values, $\varepsilon(Nd) = -10$ to -17 is taken from the literature (see text) 900 and is indicated by the green shaded region. The $\varepsilon(Nd)$ values assumed for the depleted mantle 901 range from the average MORB value (ϵ (Nd) = 8.5) to lower, less depleted values that might 902 represent an integrated depleted mantle reservoir incorporating both MORB and OIB sources, 903 ϵ (Nd) = 5, 4, 3, 2. If the depleted mantle occupies a mass fraction of = 0.6 to 0.8 (blue shaded 904 region), the $\varepsilon(Nd)$ value of such an integrated MORB+OIB reservoir would have to be 905 unrealistically low (ϵ (Nd) \leq 3.5). This is inconsistent with observed ϵ (Nd) values of average 906 MORB (8.5), average OIB (4.4), and Oceanic plateaus (5.8); see also Fig. 6.

907

908 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, 916 specifically including Th and U, end up with (physically impossible) negative concentrations in 917 the depleted mantle for both bulk crustal compositions. This provides additional, independent 918 evidence that conventional, ε (Nd)-derived crust-mantle mass balances are based on incorrect 919 assumptions.

920

921

922 Fig. 6.

923 Histogram of ε (Nd) values of mid-ocean ridge segment averages (Gale et al., 2013) and a new 924 compilation of oceanic hotspot averages (Table S4, Supplementary Information). The hotspots 925 selected for this compilation are those listed by Sleep (1990), for which published ϵ (Nd) data 926 exist. Each hotspot average represents the average value of individual volcano averages 927 belonging to a given hotspot. The particular volcanoes selected are in some cases, such as 928 Iceland, incomplete and somewhat arbitrary; they are largely governed by the availability of 929 data. We also note that the hotspot averages have not been weighted for the plume flux given 930 by Sleep (1990). We suggest that, given the existing sampling of hotspots, a perfectly 931 representative distribution of hotspot isotopic compositions is probably not possible at the 932 present time.

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936 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.

947

Fig. 8.

948Spidergrams of the trace element contents of the Early Enriched and Early Depleted Reservoirs949(EER and EDR). This model is based on extracting an early-formed batch melt (melt fractions F =9500.10 and 0.12) and storing a mass fraction of $X_{EER} = 0.02$ or 0.03 as a hidden EER at the base of951the mantle. These parameters are chosen to yield present-day ε (Nd) values close to +3.5, the952minimum needed to explain the high ε (Nd) values of present-day MORB+OIB reservoirs after953subsequent extraction of the continental crust from an early-depleted mantle. Partition954coefficients given by SS - Salters and Stracke (2004) and WH - Workman and Hart (2005).

955

956 Fig. 9.

957 Isotopic evolution, shown as $\varepsilon(Nd)$ vs. age, of EDR (Early-Depleted Reservoir, solid green line), 958 the complementary EER (dotted green line). For clarity, the green lines show only one of the 959 three versions of the complementary EER – EDR differentiation, namely the one corresponding 960 to the red line shown in Fig. 8. Without further differentiation, ε (Nd) of the EDR would increase 961 to a value of about +3.5 at the present time. In addition, we show three crust-mantle evolution 962 trajectories, corresponding to three estimates of bulk crustal composition (yellow: Hacker et al., 963 2015; red: McLennan et al., 2006; blue: Rudnick & Gao, 2003). The specific case illustrated here 964 corresponds to one of the solutions shown in Fig. 10 where the entire EDR is involved in the 965 generation of continental crust. In addition, for clarity of illustration, we assume that all crust 966 extraction took place as a single event 2 Ga ago. In this simplified scenario, the present-day 967 isotopic composition of the continental crust coincidentally matches that of the EER 968 approximately.

969

970

971

973 Fig. 10.

974 Final crust-mantle mass balance of the four-reservoir Earth showing the mass fraction of the 975 residual mantle as a function of the U content of the bulk continental crust. In this mass balance 976 the primitive mantle has been replaced by the Early-Depleted Mantle (EDR) shown in Fig. 8, 977 which is then differentiated into continental crust and Residual Mantle. Again, the specific 978 version of EDR chosen corresponds to the red line in Fig. 8. To explore how sensitive the results 979 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 980 981 those for $(Nb/U)_{rm}$ = 42 and 50, which incorporate possible uncertainties somewhat beyond 982 those for MORB data alone, and covering the majority of aberrant OIB data. For the preferred 983 crustal U concentrations of 1.1 to 1.3 ppm and the MORB average Nb/U = 46, the mass fraction 984 of the residual mantle, X_{rm} , ranges from 0.8 to 0.98. The corresponding residual mantle 985 fractions for $(Nb/U)_{rm}$ = 42 and 50 would be X_{rm} = 0.94 to 1.0 (>1 is physically impossible), and 986 0.75 to 0.9, respectively.

987

988

989 Fig.11.

990 Incompatible trace element contents of the Early-Depleted mantle and three versions of the 991 Residual Mantle, computed for $(Nb/U)_{rm} = 46$ and three popular versions of the composition of 992 the bulk continental crust, RG (Rudnick & Gao, 2003) containing 1.3 ppm U which require a high 993 value of X_{rm} = 0.97, HKB (Hacker et al., 2015) containing 1.14 ppm U, and corresponding to an 994 intermediate value of X_{rm} = 0.9, and MTH (McLennan et al., 2006) containing 1.1 ppm U, 995 corresponding to a relatively low value of X_{rm} = 0.8. All three crustal estimates lead to 996 remarkably similar compositions of the residual mantle (also compare Table 1). For the heat 997 producing elements Th and U, the discrepancies generated by the different crustal estimates do 998 not exceed 20%. All of the newly estimated residual mantle compositions are substantially less 999 depleted than currently used estimates given by Salters and Stracke (2004) and Workman and 1000 Hart (2005), which were based on radiogenic isotopes and the conventional three-reservoir 1001 crust-mantle differentiation model.

1003 Fig.12.

1004 Cartoon of a possible crust-mantle evolution consistent with the constraints imposed by the 1005 combined evaluation of ϵ (Nd) and (Nb,Ta)/U-based mass balances. (a) Initial differentiation of 1006 the primitive mantle into an EER (Early-Enriched Reservoir) by forming and subducting a mafic 1007 early (possibly primordial) crust, leaving behind a slightly depleted Early Depleted mantle (EDR) 1008 with primitive (Nb,Ta)/U but fractionated Sm/Nd. (b) Subsequent differentiation of the EDR into 1009 continental crust having Nb/U = 7 and a Residual Mantle Reservoir (RM) having Nb/U = 46. In 1010 this particular version, the RM occupies all of the mantle except the EER, but the uncertainties 1011 of the model allow up to about 20% EDR surviving in the mantle. Present day mantle: the 1012 residual mantle has undergone additional differentiation into MORB and OIB sources, and the 1013 EER has accumulated in the two LLSVPs in the lowermost mantle. 1014

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
Ва	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
Nb1	0.555	0.8215	8.00	8.00	8.10	14.41	14.41	14.59	0.738	0.720	0.731
Та	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. 2



Fig. 3









Fig. 5



Fig. 6



Fig. 7

1022



Fig. 8



Fig. 9



1.3 Mass Fraction of Residual Mantle 1.2 physically 1.1 impossible 1.0 0.9 ■ Nb/U = 42 0.8 • Nb/U = 46 0.7 preferred ♦ Nb/U = 50 cont. crustal 0.6 U = 1.1 – 1.3 ppm 0.5 0.8 0.9 1.1 1.2 1 1.3 1.4 U (ppm) in Continental Crust







Fig. 12

1	Supporting Information for
2	
3	Size and composition of the residual and depleted mantle reservoir
4	
5	A.W. Hofmann ^{1,2} , C. Class ¹ , S. L. Goldstein ¹
6	
7	
8	Figure Captions for Supplementary Figures
9	
10	Fig. S 1. Log U vs log Nb and log Ta for global MORB data. Slopes have been calculated
11	from two-error regression analysis assuming equal error on both axes (see also Table S1). The
12	concentrations values are normalized to the Primitive Mantle values given by McDonough and
13	Sun {, 1995 #16}. (a) Data for about 400 MORB segment averages from Gale et al. {, 2013 #12}.
14	(b) MORB glass data from Jenner and O'Neill {, 2012 #25}. (c) MORB data given by Arevalo and
15	McDonough {, 2010 #26}.
16	
17	Fig. S 2a. Slopes of log-log regressions such as those shown in Fig. S1 for logarithms of
18	Ba, Th, U, Ta, K, La versus log Nb (in the abscissa). The slopes are listed in Table S1. (2b) Same as
19	(a), but using the logarithms of Ba, Th, Nb, U, K, La, versus log Ta. The plots show that all three
20	data sets give remarkably similar results: The slope of log U vs. log Nb is slightly below 1.0,
21	whereas the slope of log U vs. log Ta is slightly greater than 1.0. From these slopes we infer the
22	following order of increasing compatibility; Ba < Th < Nb < U < Ta <k <="" la.<="" td=""></k>
23	
24	Fig. S3. Nb/Th vs Nb in MORB {Gale, 2013 #12}, oceanic plateaus, normal and HIMU-
25	type OIBs, and EM-type OIBs, in addition to values for the primitive mantle {McDonough, 1995
26	#16} and average continental crust {Rudnick, 2003 #14}. This plot shows that, although Nb/Th
27	ratios are not strictly "canonical" in that they vary systematically as a function of global
28	enrichment/depletion, their ratios in OIBs and oceanic plateaus are similarly complementary to

the continental crust as MORB values. EM-type OIBs appear to deviate systematically from the general MORB-OIB-oceanic plateau array toward somewhat lower values, presumably because they contain small amounts of recycled continental material. The OIB data are listed in Table S4.

Fig. S4. Comparison of the ALL MORB average given by Gale et al. {, 2013 #12} with partial melts of the Depleted Mantle of Workman and Hart {, 2005 #20}, using equilibrium batch melting and aggregate fractional melting. A melt fraction F = 0.03 and a final enrichment of the melt by fractional crystallization, increasing the final trace element concentrations by a factor of 1.35, following Su and Langmuir {, 2002 #70}, generates a final melt closely resembling the ALLMORB average of Gale et al {, 2013 #12}. A melt fraction of F = 0.03 is substantially lower than any of the published estimates of melt fractions involved in generating MORB.

Fig. S5. Generating MORB (ALLMORB average of Gale et al, 2013) by partially melting the Residual Mantle (RM) derived in this paper. The specific version of RM is based on the crustal average of Rudnick and Gao (2003), X(RM) = 0.974 (see Table 1). As shown in Fig. S4, batch melts and aggregate fractional melts yield similar results, but the melt fraction is significantly higher, F = 0.09 and a final factor of 1.35.

≈ 600 MORB Glasses

Jenner & O'Neill, 2012





About 400 MORB segment averages

Gale et al. 2013



Fig. S1a



Arevalo & McDonough, 2010

















Partial Melts of DM Mantle (Workman-Hart; F = 0.03, M = 1.35)

Fig. S4

Partial Melts of Residual Mantle (X_{res} = 0.97, F = 0.09, M = 1.35)

Fig. S5

Table S1

MORB: Two-error regression results

Reference	х	Y	Slope	Error	Intercept	х	Y	Slope	Error	Intercept
Gale et al. 2013	log Nb	log Ba	1.231	0.023	-0.435	log Ta	log Ba	1.314	0.028	-0.603
Jenner-O'Neill. 2012	log Nb	log Ba	1.208	0.017	-0.445	log Ta	log Ba	1.271	0.018	-0.524
Arevalo-McDonough, 2010	log Nb	log Ba	1.229	0.014	-0.475	log Ta	log Ba	1.309	0.016	-0.627
Gale et al. 2013	log Nb	log Th	1.076	0.021	-0.303	log Ta	log Th	1.137	0.025	-0.437
Jenner-O'Neill. 2012	log Nb	log Th	1.045	0.015	-0.303	log Ta	log Th	1.094	0.016	-0.369
Arevalo-McDonough, 2010	log Nb	log Th	1.075	0.013	-0.303	log Ta	log Th	1.151	0.014	-0.463
Gale et al. 2013	log Nb	log U	0.976	0.020	-0.125	log Ta	log U	1.032	0.023	-0.246
Jenner-O'Neill. 2012	log Nb	log U	0.969	0.015	-0.124	log Ta	log U	1.016	0.016	-0.185
Arevalo-McDonough, 2010	log Nb	log U	0.983	0.012	-0.114	log Ta	log U	1.034	0.014	-0.220
Gale et al. 2013	log Nb	log Ta	0.947	0.026	0.115	log Ta	log Nb	1.056	0.023	-0.121
Jenner-O'Neill. 2012	log Nb	log Ta	0.956	0.014	0.058	log Ta	log Nb	1.047	0.015	-0.061
Arevalo-McDonough, 2010	log Nb	log Ta	0.942	0.012	0.102	log Ta	log Nb	1.061	0.014	-0.109
Gale et al. 2013	log Nb	log La	0.695	0.017	0.282	log Ta	log La	0.724	0.020	0.200
Jenner-O'Neill. 2012	log Nb	log La	0.694	0.013	0.270	log Ta	log La	0.730	0.013	0.225
Arevalo-McDonough, 2010	log Nb	log La	0.699	0.010	0.296	log Ta	log La	0.748	0.012	0.216

Table S1. Two error regression results of log-log plots for 3 datasets representing global MORB

Table 1 Footnote: Two-error regressions were calculated using ProFit software package, assigning equal errors to x and y values and no weighting of data.

The log-log slopes of Nb vs. U are slightly but consistently lower than 1.0 (= 0.969 to 0.983).The log-log slopes of Ta vs. U are slightly but consistently greater than 1.0 (= 1.016 to 1.034).An element having partitioning properties between Nb and Ta would yield a slope equal to 1.0Table S1

Average MORB										Calc	Calc	
ratios	Nb/U	Nb/U	Nb/U	Ta/U	Ta/U	Ta/U	Nb/Th	Nb/Th	Nb/Th	Nb/Ta	Th/U	
	Ave	Std Dev	Variability	Ave	Std Dev	Variability	Ave	Std Dev	Variability			Γ
Jenner & O'Neill,												
2012	46.1162	7.4737	0.1621	2.7479	0.4360	0.1587	15.6981	2.5522	0.1626	16.78	2.94	
Gale et al., 2013;												
segment aves	46.139	9.212	0.200	3.088	0.672	0.217	14.876	3.017	0.203	14.94	3.10	
Arevalo &												ľ
McDonough, 2010	44.852	10.302	0.230	2.909	0.625	0.215	16.187	4.241	0.262	15.42	2.77	

Comparison of Averages, Std. Deviations, Variabilities of Nb/U, Ta/U, and Nb/Th

Table S2. Average Nb/U, Ta/U, Nb/Th, Nb/Ta, and Th/U ratios for the three data sets indicated by the references and used in Table 1 and Figs. S1 and S2. Note that the Ta/U ratio (= 2.75) calculated from the data of Jenner and O'Neill (2012) appears to be systematically lower than the values given by the other two references. This low Ta/U value corresponds to a significantly higher Nb/Ta ratio of 16.78 compared with Nb/Ta = 14.94 and 15.42 obtained by the other two groups. Jenner and O'Neill (2012) also report a somewhat anomalously low Ta value for the standard reference glass BCR-2G (6.7% lower than the recommended GeoReM value). For reasons of internal consistency, we will not use the Ta/U value for average MORB given by Jenner and O'Neill (2012), but rely on the Ta/U value of Gale et al. (2013)

Table S2

U	Th	Nb	Ta	Reference
0.91	4.20	11.0	1.00	Taylor and McLennan, 1985
1.40	5.6	8.0	0.70	Rudnick and Fountain, 1995
1.10	4.20	8.0	0.80	McLennan et al. 2006
1.30	4.20	8.0	0.70	Rudnick and Gao, 2003
1.13	4.29	7.4	0.54	Hacker et al., 2015
1.10	4.23	7.4	0.52	Hacker et al., 2015
1.09	4.20	8.1	0.52	Hacker et al., 2015
1.33	5.31	8.8	0.55	Hacker et al., 2015
1.14	4.29	8.1	0.53	Hacker et al., 2015

Table S3. Literature data for estimates of trace element concentrations for U, Th, Nb, Ta in the continental crust

Table S3