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Chemical composition of Earth's primitive mantle and its variance:
2. Implications for global geodynamics

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[1] The global budgets of argon and heat-producing elements have traditionally been used to argue for layered-mantle convection because they require a large fraction of Earth's mantle to remain isolated from mantle convection. We revise these mass balance arguments using our new composition model of the primitive mantle and show that the global budgets of argon, heat-producing elements, and rare earth elements are consistent with Earth's mantle almost entirely composed of the mid-ocean ridge basalt source mantle, supporting the notion of whole mantle convection. Combined with a recent theory on the thermal evolution of Earth, our revised thermal budget implies inefficient mixing and processing in the past, explaining the survival of long-lived geochemical heterogeneities in convecting mantle.

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1. Introduction

[2] The structure of mantle convection has been one of the most controversial subjects in modern geodynamics and geochemistry. Geophysical data provide a strong support for whole mantle convection. In particular, the seismological observations of mantle plumes coming from the deep mantle and subducting slabs penetrating the 660 km discontinuity indicate significant mass transport between the upper and the lower mantle [*Fukao et al.*, 2001; *van der Hilst et al.*, 1997; *Montelli et al.*, 2004]. Dynamical constraints derived from numerical modeling of Earth's geoid also favor whole mantle convection [e.g., *Hager et al.*, 1985]. As suggested by the numerical modeling of mantle mixing, whole mantle convection could lead to considerable homogenization of Earth's mantle [e.g., *Olson et al.*, 1984; *Ferrachat and Ricard*, 1998; *van Keken et al.*, 2002]. A number of geochemical arguments, however, indicate the existence of geochemical heterogeneity that has been preserved in Earth's mantle despite convective stirring [e.g., *Hofmann*, 1997].

[3] A crucial question for mantle dynamics is the size of such heterogeneity. Whereas the preservation of a massive mantle reservoir with distinct chemical composition is hard to reconcile with the whole mantle convection model, small-scale heterogeneities may still survive in convecting mantle if mixing is inefficient. Among a number of geochemical arguments that have been used to favor layered-mantle convection, it is global mass balance calculations that can constrain the size of an isolated mantle reservoir. Other arguments do not provide a robust constraint on the size of such a hidden reservoir, because the interpretation of geochemical data is often model-dependent. For example, observed geochemical differences between mantle-derived basalts erupting at mid-ocean ridge basalts (MORBs) and those from oceanic island basalts (OIBs) may simply be explained by differences in mantle flow and lithospheric thickness as suggested by *Sleep* [1984] and more recently by *Ito and Mahoney* [2005], without calling for an isolated, large-scale mantle reservoir.

[4] There are a few different arguments based on global mass balance, and among them, the "missing argon" paradox is regarded as most important by many geochemists because it appears to require the isolation of a large fraction (up to 50%) of mantle mass from convection [e.g., *Allègre et al.*, 1996; *Lassiter*, 2004]. This paradox is based on the discrepancy between the observed amount of ^{40}Ar in Earth's main reservoirs (i.e., the atmosphere, the continental crust, and the depleted mantle) and the predicted ^{40}Ar produced by K in the bulk silicate Earth. *Allègre et al.* [1996] argued that depleted mantle, continental crust, and atmosphere together can only account for about 50% of total argon budget. Since it is extremely unlikely that the core can contain any argon [*Chabot and Drake*, 1999], mass balance considerations require the existence of a large, relatively undegassed mantle reservoir. *Porcelli and Turekian* [2003] suggested that a similar argument can also be made based on the global inventory of radiogenic ^{136}Xe, but this argument is much less certain because the amount of radiogenic xenon in the atmosphere is hard to evaluate [e.g., *Porcelli and Pepin*, 2003], and the loss of xenon into space during Earth's early intensive degassing cannot be neglected [e.g., *Halliday*, 2003; *Porcelli and Turekian*, 2003].

[5] Another constraint on the mantle structure comes from the budget of the heat-producing elements, K, U,

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and Th, in the bulk silicate Earth. There are several different formulations of this problem [e.g., *O'Nions et al.*, 1978; *O'Nions and Oxburgh*, 1983; *Turcotte et al.*, 2001], all of which result in a similar conclusion that the continental crust and the depleted MORB source together cannot account for the bulk Earth abundance of the heat-producing elements (HPEs), and an additional mantle reservoir storing the remaining HPEs is required. Mass balance calculations for incompatible lithophile elements have also been used to indicate that a mantle reservoir enriched in incompatible elements is needed to complement the depleted mantle and continental crust [e.g., *Helffrich and Wood*, 2001; *Albarède and van der Hilst*, 2002].

[6] Note that all of these mass balance arguments are based on negative results. The failure to construct a self-consistent chemical model of the silicate Earth based on the compositions of the primitive mantle, MORB source mantle, and continental crust has been used as a major argument for the existence of a hidden reservoir in Earth's mantle. Such proofs by contradiction would not be trustworthy, however, unless the contradiction is beyond dispute. In global mass balance, all kinds of present-day silicate reservoirs should sum up to the primitive mantle, but its composition cannot be measured directly today. We thus have to somehow estimate its composition, and the robustness of mass balance arguments relies on how it is estimated.

[7] In our companion paper we reviewed previous models for the primitive mantle (PM) composition and presented a new PM composition model based on by far the most comprehensive statistical analysis of mantle peridotites. Our model is depleted in a number of trace elements, and as we will show in this paper, this model eliminates the previous discrepancy in the budget of argon, HPEs, and lithophile elements. This self-consistent global mass balance is important because it supports the global-scale homogeneity of Earth's mantle, which is assumed in our model (as well as any other pyrolite-type models based on the analysis of upper mantle peridotite compositions). Although we do not have any direct sample from Earth's lower mantle, there is also no particular evidence suggesting that its composition is grossly different from that of the upper mantle (see section 5). With the successful closure of global mass balance, we finally have a self-consistent chemical model for the silicate Earth.

[8] In sections 2–5 we will present the calculation of the argon budget (section 2), the thermal budget (section 3), and the budget of lithophile elements (section 4) based on the new PM model. The emerging picture of the mantle structure (Figure 1) will be discussed in section 5.

2. Earth's Argon Budget

2.1. "Missing Argon" Paradox

[9] ^{40}Ar is predominantly produced by the decay of ^{40}K. The high atomic weight prevents it from escaping Earth's atmosphere. Moreover, due to the relatively large half-life of ^{40}K, intensive degassing, which probably occurred early in Earth's history, has had only minor effect on the global budget of ^{40}Ar. Therefore it can be safely assumed that all of ^{40}Ar produced by ^{40}K decay over Earth history should be stored among various reservoirs in Earth.

[10] The amount of ^{40}Ar produced over Earth's history can be determined from the present-day concentration of ^{40}K in the bulk Earth:

$$^{40}\mathrm{Ar} = \frac{\lambda_e}{\lambda}\,^{40}\mathrm{K}\left(e^{\lambda t} - 1\right),$$

where $\lambda = \lambda_\beta + \lambda_e$, λ_β and λ_e are the decay constants for beta decay and electron capture, respectively, and t is time [*Dickin*, 2005]. For a particular reservoir with a certain age t the amount of ^{40}Ar generated is thus a linear function of K abundance in this reservoir. Earth's budget of ^{40}Ar is therefore predetermined by the estimate of K abundance for the bulk Earth and those for the mantle and the crust.

[11] The first attempt to evaluate Earth's budget of ^{40}Ar was made by *Turekian* [1959]. The bearing of ^{40}Ar budget on mantle structure has been emphasized particularly by *Allègre et al.* [1996]. They estimated the amount of ^{40}Ar produced in the bulk silicate Earth over 4.5 Ga at 140–156 $\times$ 10^{18} g, based on the BSE K abundance of 250–285 ppm (see Table 1). Argon has been constantly released into the atmosphere through volcanic degassing, and Earth's atmosphere today contains approximately 66 $\times$ 10^{18} g of ^{40}Ar [*Turekian*, 1959]. The remaining ^{40}Ar must therefore still remain within the silicate Earth. However, the combined estimate of the ^{40}Ar mass contained in the continental crust and the MORB source mantle is only about 30–50% of ^{40}Ar stored within Earth's interior (i.e., the difference between the total ^{40}Ar production and the amount of ^{40}Ar contained in the atmosphere). Consequently, mass balance considerations require an additional reservoir much richer in ^{40}Ar than the depleted upper mantle:

$$M\left(^{40}\mathrm{Ar}\right)_{BSE} = M\left(^{40}\mathrm{Ar}\right)_{atm} + M\left(^{40}\mathrm{Ar}\right)_{CC} + M\left(^{40}\mathrm{Ar}\right)_{DM} + M\left(^{40}\mathrm{Ar}\right)_{hidden}.$$

[12] Since Earth's budget of ^{40}Ar is determined by K abundance in Earth's reservoirs and in the bulk Earth, this discrepancy in argon budget should merely reflect the inconsistency of potassium budget. In Table 1 the calculation of Earth's potassium budget based on the work by *Allègre et al.* [1996] is presented. Clearly, the continental crust and the depleted mantle together can account for only about ~50% of the bulk Earth potassium budget. Although there have been some debates regarding the possibility of K partitioning into the core [e.g., *Lodders*, 1995; *Gessmann and Wood*, 2002], various geochemical evidence seem to indicate only negligible amount or no heat-producing elements in the core (see *McDonough* [2003] for detailed discussion). The deficit of potassium in Earth is therefore translated into about 50% deficit of argon.

[13] The concentrations of K in the continental crust and the depleted mantle are reasonably well constrained by compositions of crustal rocks and MORBs. The bulk Earth K concentration, however, is usually derived from the primitive mantle concentration of U and the bulk Earth K/U ratio [e.g., *McDonough and Sun*, 1995; *Allègre et al.*, 2001; *Palme and O'Neill*, 2003]. The bulk Earth K/U ratio is unknown, but relatively small variations of K/U in

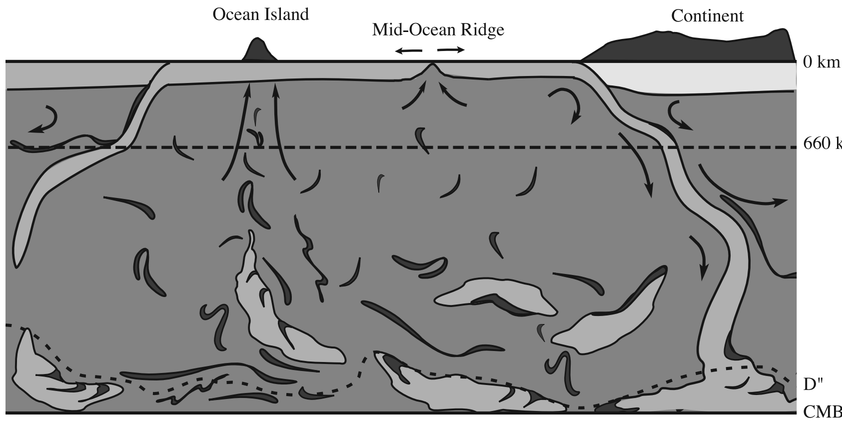

Figure 1. Illustration of our preferred model for the structure of Earth's mantle, based on the new BSE model and mass balance calculations. Dark shading is used to indicate chemical composition enriched in incompatible elements (as a result of melting); light shading corresponds to depleted composition. Dark shaded fragments denote subducted oceanic crust. No vertical stratification in chemical composition is required by global mass balance for argon and heat-producing elements (sections 2 and 3). Most of the mantle is expected to have the MORB source composition, although large uncertainties in compositional models for the bulk silicate Earth and continental crust allow for the existence of some small-scale mantle heterogeneity (section 4). The subducted oceanic lithosphere stored within the mantle is a likely candidate for the source of the small-scale mantle heterogeneity. Anomalies in seismic wave velocity and scattering of seismic energy suggest the existence of lateral variations in the major element composition of the lower mantle (section 5.2). Those lateral variations are likely to be produced by the remnants of subducted slabs, which have their bulk chemical composition different from that of surrounding mantle. The distinct geochemical signature of OIB can be explained by subducted oceanic lithosphere of various ages [e.g., *Lassiter and Hauri*, 1998], as well as by differences in mantle flow and lithospheric thickness between mid-ocean ridges and hot spots [e.g., *Ito and Mahoney*, 2005]. Earth's budget of heat-producing elements and petrological data on the degree of Earth's secular cooling require more sluggish mantle convection in the past (section 3.2). Sluggish mantle convection may explain the presence of long-lived mantle heterogeneity as well as the primordial noble gas signature of MORB and OIB in the context of whole mantle convection.

Table 1. Argon Budget Calculation

Parameter	*Allègre et al.* [1996]	*Lassiter* [2004]	This Study
U concentration in the BSE, ppb	20–22.5	21	14.3–20.3
Constraint on K abundance in BSE	K/U ~ 12,700	K/U ~ 7,000–9,000	K/U ~ 12,700, K/La ~ 330
K concentration in the BSE, ppm	250–285	150–195	150–230
K mass in the BSE, g × 10^{23}	10.2–11.6	6.1–7.9	6.1–9.4
^{40}Ar produced in the BSE over 4.5 Ga, g × 10^{18}	140–156	84–110	83–127
^{40}Ar stored in the atmosphere, g × 10^{18}	66	66	66
^{40}Ar stored in the present-day solid Earth, g × 10^{18}	74–90	18–44	17–61
K concentration in the continental crust, %	1.7–2.0	1.56	1.0–2.0
K mass in the continental crust, g × 10^{23}	4.0–4.7	3.8	2.4–4.7
Mean age of the continental crust, Ga	2.0–2.7	1.7	1.7–2.9
^{40}Ar produced in the continental crust, g × 10^{18}	10–20[a]	8.7	5–23
Present-day ^{40}Ar flux from the continental crust, g × 10^{9} yr^{-1}	not specified	-	2.5–4.8
^{40}Ar outgassed from the continental crust over its history, g × 10^{18}	5–10	not specified	4–14
^{40}Ar stored in the continental crust, g × 10^{18}	5–10[a]	<8.7	1–9
K concentration in the MORB source mantle, ppm	40–50	-	40–80
K mass in the MORB source mantle, g × 10^{23}	1.7–2.1	-	1.7–3.1
^{40}Ar produced in the MORB source mantle over 4.5 Ga, g × 10^{18}	22–28	-	23–45
Present-day ^{40}Ar flux from mid-ocean ridges, g × 10^{8} yr^{-1}	2.5–19	29	0.4–36
^{40}Ar outgassed from the MORB source mantle over 4.5 Ga, g × 10^{18}	-	-	0.2–16
^{40}Ar stored in the MORB source mantle, based on K abundance, g × 10^{18}	<28	not specified	6–43[b]
^{40}Ar stored in the MORB source mantle, based on ^{40}Ar flux, g × 10^{18}	1.8–13a	2–18	0.2–25[b]

[a]Estimates are derived based on parameters stated by *Allègre et al.* [1996]; discrepancies between values given here and those in the original paper should be due to lower precision or typos by *Allègre et al.* [1996].

[b]These two estimates are inversely correlated, and our best estimate is 10–20 × 10^{18} g (see text for details).

MORBs and continental rocks indicate that K and U have similar incompatibilities during melt extraction, and the bulk Earth K/U ratio should be close to that in the continental and oceanic crust [e.g., *Jochum et al.*, 1983].

[14] *Albarède* [1998] and *Davies* [1999] proposed that the "missing argon" paradox could be resolved by postulating a ~50% lower K/U ratio in the bulk Earth. A recent paper by *Lassiter* [2004] suggests that recycled oceanic crust stored in Earth's mantle may lead to a lower K/U ratio in the bulk Earth than commonly estimated. The lower estimate of K/U is, however, highly sensitive to the amount of recycled eclogite, which is at present unconstrained. In addition, *Porcelli and Turekian* [2003] argue that large deviations from the bulk Earth K/U value of ~12,000 may not be compatible with the cosmochemical volatility trend in the K/U vs. Rb/Sr space [*Halliday and Porcelli*, 2001] (though this argument is subject to large uncertainty [*Lassiter*, 2004]).

[15] In our companion paper we derived a new estimate of the bulk Earth concentration of potassium at ~190 ppm, which is significantly lower than the commonly used value of ~240 ppm [*McDonough and Sun*, 1995]. This difference arises from our lower estimate of the U concentration in the BSE at ~17.3 ppb. The possibility of recycled crust stored in Earth's mantle may lead to an even lower estimate of K because our estimate is based on the conservative value of the bulk Earth K/U ratio (as well as K/La ratio). Our new value for the bulk Earth K abundance, combined with recent composition models for the continental crust [*Rudnick and Gao*, 2003] and the depleted mantle [*Salters and Stracke*, 2004], results in a self-consistent potassium budget with no need for any additional K-rich reservoir. A corresponding argon budget also supports a notion of a large-scale mantle homogeneity, thus eliminating one of the major arguments for layered-mantle convection.

[16] In sections 2.2–2.4 we present the details of the calculations of ^{40}Ar budgets in the continental crust, the MORB source mantle, and the bulk Earth. Table 1 summarizes important steps in the calculations and results derived in this study, in comparison to those obtained by *Allègre et al.* [1996] and *Lassiter* [2004].

2.2. Argon Budget in Continental Crust

[17] There are a number of studies on the average chemical composition of the continental crust [e.g., *Taylor and McLennan*, 1985; *Rudnick and Fountain*, 1995; *Taylor*, 1995; *McLennan and Taylor*, 1996; *Gao et al.*, 1998]. Most of estimates on crustal K abundance vary from ~1.1 to ~1.9%. A recent study by *Rudnick and Gao* [2003] evaluates the crustal potassium concentration at 1.5% with the uncertainty of ~0.5%. In this study therefore we will consider crustal K abundance to be in the broad range of 1.0–2.0%.

[18] To determine the corresponding amount of ^{40}Ar generated in the crust requires certain assumptions about the crustal age. The age of continental crust is one of the largest uncertainties in crustal argon budget. There has been considerable discussion about the formation time and early production rate of the continental crust. Various growth curves have been proposed, from slow steady growth based on K-Ar ages [e.g., *Hurley and Rand* 1969] to rapid early growth [e.g., *Armstrong*, 1981; *Bowring and Housh*, 1995], and various intermediate histories [e.g., *Nelson and DePaolo*, 1985; *Condie*, 1990].

[19] A mean K-Ar age of the crust based on steady progressive crustal growth is determined at ~1 Ga [*Hurley and Rand*, 1969]. However, the current rate of crustal formation is ~1 km^3 yr^{-1} [*Reymer and Schubert*, 1984], which is insufficient to generate the full mass of the crust over 4.5 Ga [*Porcelli and Turekian*, 2003]. Clearly, crustal formation was more rapid in the past, and the mean age of continental crust must be substantially older than the K-Ar age. The crustal growth models based on Sm-Nd systematics lead to a greatly increased estimate of the rate of Lower Proterozoic crustal growth, with the corresponding estimate of the average age of the continental crust at 1.7 ~ 1.9 Ga [e.g., *Nelson and DePaolo*, 1985; *Patchett and Arndt*, 1986]. Alternative models involving early Earth differentiation and rapid early crustal growth suggest that the average age of the continental crust may be even older, and most of the crustal volume may have already been accreted as early as 2.9 Ga [e.g., *Armstrong*, 1981; *Campbell*, 2003]. For this study therefore we use the range of 1.7–2.7 Ga as possible crustal ages. Combined with the crustal K abundance of 1.0–2.0%, this results in 5–23 × 10^{18} g of ^{40}Ar generated in the continental crust. However, much of the ^{40}Ar produced in the crust might have escaped into the atmosphere, and the amount of ^{40}Ar stored within the crust is likely to be significantly less than this estimate.

[20] We can approximately evaluate the amount of ^{40}Ar degassed from the continental crust over its history based on the estimates of present-day crustal flux of ^{40}Ar. Although this flux cannot be measured directly, it can be inferred from the measurements of dissolved argon in ground waters, rates of potassium discharge into the oceans due to chemical weathering of crystalline rocks, and estimated ^{40}Ar release in thermal processing due to tectonic thickening of the crust in orogenic belts [*Porcelli and Turekian*, 2003]. In summary, the total continental flux equals about 2.5–4.8 × 10^9 g yr^{-1}. Assuming this flux for the whole history of continental crust yields the amount of the outgassed argon 4–14 × 10^{18} g of ^{40}Ar.

[21] Finally, the amount of argon stored in the present-day crust can be roughly estimated as the difference between the amount of argon produced and degassed out of the crust. Using the above values, we evaluate the amount of argon stored in the crust at 1–9 × 10^{18} g, which is comparable to the estimates of *Allègre et al.* [1996] (5–10 × 10^{18} g) and *Lassiter* [2004] (<8.7 × 10^{18} g, Table 1).

2.3. Argon Budget in the MORB Source Mantle

[22] The amount of argon stored in the present-day depleted mantle can be estimated using two approaches. First, the concentration of potassium in the MORB source mantle can be used to calculate the amount of ^{40}Ar produced in the depleted mantle over its geological history. As mantle is being constantly degassed in mid-ocean ridges, the amount of ^{40}Ar stored in the depleted mantle can be evaluated as the difference between ^{40}Ar produced in the mantle and that outgassed into the atmosphere. A considerable uncertainty in this approach is the regime of mantle degassing during Earth's history. High ^{40}Ar/^{36}Ar ratios measured in MORB require very intensive mantle degassing in the first several million years, followed by a

continuous release until today [e.g., *Hamano and Ozima*, 1978; *Sarda et al.*, 1985]. The early intensive degassing, however, should not have significantly affected the mantle ^{40}Ar abundance due to its radiogenic origin. A conservative estimate for the amount of ^{40}Ar outgassed from the mantle may thus be obtained by assuming that ^{40}Ar flux has been constant over the geological history and equal to the present-day flux at mid-ocean ridges.

[23] Second, the present-day flux of ^{40}Ar at mid-ocean ridges can be used to obtain a more direct estimate of the ^{40}Ar stored in the depleted mantle, as the present-day flux directly reflects the concentration of argon in the mantle material. The mass of the oceanic mantle passing through the ridge system is $\sim 5.7 \times 10^{17}$ g yr^{-1}, assuming that mantle starts to melt at ~60 km depth, the mean density of the mantle is 3.2 g cm^{-3} and the rate of oceanic plate production is ~3 km^2 yr^{-1}. If argon is completely extracted from the partially molten mantle, then ^{40}Ar concentration in the depleted mantle is determined as a ratio of ^{40}Ar flux to the mass of the processed mantle.

[24] The estimates of K abundance in the MORB source suggested by previous authors vary from 40 to 100 ppm [*Jochum et al.*, 1983; *Salters and Stracke*, 2004; *Workman and Hart*, 2005; *Korenaga*, 2006]. The upper limit of this interval corresponds to the estimate derived from the composition of primary mantle-derived melts [*Korenaga and Kelemen*, 2000; *Korenaga*, 2006]. For this calculation we adopt a conservative estimate of 40–80 ppm for MORB source K content, which is consistent with the preferred estimates of *Jochum et al.* [1983], *Salters and Stracke* [2004], and *Workman and Hart* [2005]. Assuming that the MORB source mantle constitutes the entire mantle, the amount of ^{40}Ar produced over 4.5 Ga thus belongs to an interval of $23–45 \times 10^{18}$ g. This is broader than the estimate made by *Allègre et al.* [1995] ($23–28 \times 10^{18}$ g) due to their use of 40–50 ppm for the K abundance in the MORB source mantle (Table 1).

[25] The flux of ^{40}Ar at mid-ocean ridges cannot be measured directly, since ^{40}Ar in most hydrothermal fluids is dominated by atmospheric argon. Instead, the concentration of ^{3}He in oceanic water is used to estimate ^{3}He flux at mid-ocean ridges [e.g., *Craig et al.* 1975], and then the ^{4}He/^{3}He and ^{4}He/^{40}Ar ratios in MORBs are used to infer the ^{40}Ar flux [e.g., *Allègre et al.*, 1996; *Lassiter*, 2004]. Using the estimate of ^{3}He flux at mid-ocean ridges at $\sim 1.1 \times 10^3$ mol yr^{-1} [*Craig et al.*, 1975] combined with an average MORB ratio ^{4}He/^{3}He ~ 82,000 [*Graham*, 2002], the flux of ^{4}He is approximately $\sim 9.8 \times 10^7$ mol yr^{-1}. Measured ^{4}He/^{40}Ar ratios in MORB are, however, highly variable. *Honda and Patterson* [1999] report the MORB values of ^{4}He/^{40}Ar from less than 1 to as high as 100. *Lassiter* [2004] argues that measured ^{4}He/^{40}Ar in MORB might be only an upper bound for the ^{4}He/^{40}Ar of the depleted mantle, and the noble gas ratios in popping rocks are likely to better represent the MORB source composition. The popping rock ^{4}He/^{40}Ar reported by *Moreira and Allègre* [1998] is ~1.5. As there is still a considerable uncertainty in the MORB source ^{4}He/^{40}Ar, we will explore the entire range of 1–100 ^{4}He/^{40}Ar in our calculation. This uncertainty overwhelms other sources of uncertainties, for example, associated with the mantle processing rate beneath mid-ocean ridges. Our estimate for the present-day flux of ^{40}Ar is thus within the broad interval of $0.4–36 \times 10^8$ g yr^{-1}.

[26] The above estimate of ^{40}Ar flux directly translates into $0.2–25 \times 10^{18}$ g of ^{40}Ar stored in the MORB source mantle (given $\sim 5.7 \times 10^{17}$ g yr^{-1} for the mass of the mantle processed at mid-ocean ridges). On the other hand, we can use the present-day ^{40}Ar flux to evaluate the amount of ^{40}Ar outgassed from the mantle over 4.5 Ga; the difference between ^{40}Ar produced by K decay in the MORB source mantle and that outgassed into the atmosphere yields an alternative estimate for the amount of ^{40}Ar stored in the MORB source mantle. The latter estimate of $6–43 \times 10^{18}$ g is in fact an upper bound, since more argon might have escaped the mantle due to higher degassing rates in the past. Note that the two estimates are inversely correlated; a lower Ar flux results in a higher MORB source ^{40}Ar abundance derived by the first method, and a lower one derived by the second method. The intersection of the two estimates yields the range of $10–20 \times 10^{18}$ g, which may be considered as our best guess for the ^{40}Ar abundance in the depleted mantle (Table 1).

2.4. Global Argon Budget

[27] As was mentioned above, the global budget of ^{40}Ar is a linear function of K budget. Table 1 shows the estimates of the mass of K contained in the bulk silicate Earth, the continental crust, and the MORB source mantle in the previous studies [*Allègre et al.*, 1996; *Lassiter*, 2004] and in this work. The combined budget of K in the depleted mantle and the continental crust of $5.6–6.7 \times 10^{23}$ g in the work by *Allègre et al.* [1996] is close to our estimate of $4.1–7.8 \times 10^{23}$ g. These values would be much lower than the amount of K stored in the bulk silicate Earth, $10.2–11.6 \times 10^{23}$ g, if BSE K concentration is 250–285 ppm. However, our new estimate of K abundance in the BSE at 190 ± 40 ppm results in only $6.1–9.4 \times 10^{23}$ g of K in the bulk silicate Earth, thus eliminating the inconsistency in K the budget.

[28] The corresponding amount of ^{40}Ar stored in Earth's interior is $17–61 \times 10^{18}$ g, which is lower than that estimated by *Allègre et al.* [1996] ($74–90 \times 10^{18}$ g). Our estimate for ^{40}Ar stored within the continental crust and the MORB source mantle is $11–30 \times 10^{18}$ g (Table 1). Clearly, the continental crust and the MORB source mantle together can account for the mass of ^{40}Ar that is expected to reside in the silicate Earth, with no need to assume the existence of an additional large-scale mantle reservoir. One may still claim for the existence of a hidden reservoir by noting that the ^{40}Ar content in Earth's interior could be as high as 61×10^{18} g even with our PM model, whereas the depleted mantle and the continental crust together can account for 30×10^{18} g at most. Though it is a possibility, such an argument misses entirely the crux of the "missing argon" paradox. The paradox has been considered robust because it used to be impossible to make a self-consistent mass balance. This is no longer the case.

3. Earth's Thermal Budget

3.1. Global Budget of Heat-Producing Elements

[29] The global budget of heat-producing elements based on the compositional models for the bulk silicate Earth, the

Table 2. Global Budget of Heat-Producing Elements

	Continental Crust[a]		MORB Source Mantle[b]	
Element	C, ppm	M, g	C, ppb	M, g
K	$(1.5 \pm 0.45) \times 10^4$	$(3.5 \pm 1.1) \times 10^{23}$	$(60 \pm 17) \times 10^3$	$(2.4 \pm 0.7) \times 10^{23}$
U	1.3 ± 0.4	$(3.1 \pm 0.9) \times 10^{19}$	4.7 ± 1.4	$(1.9 \pm 0.6) \times 10^{19}$
Th	5.6 ± 1.7	$(13.2 \pm 4.0) \times 10^{19}$	13.7 ± 4.1	$(5.5 \pm 1.7) \times 10^{19}$
	BSE [*McDonough and Sun*, 1995]		BSE, New Model	
Element	C, ppb	M, g	C, ppb	M, g
K	$(240 \pm 48) \times 10^3$	$(9.8 \pm 1.9) \times 10^{23}$	$(190 \pm 40) \times 10^3$	$(7.7 \pm 1.6) \times 10^{23}$
U	20.3 ± 4.1	$(8.2 \pm 1.7) \times 10^{19}$	17.3 ± 3.0	$(7.0 \pm 1.2) \times 10^{19}$
Th	79.5 ± 11.9	$(32.3 \pm 4.8) \times 10^{19}$	62.6 ± 10.7	$(25.4 \pm 4.3) \times 10^{19}$

[a]Based on work by *Rudnick and Gao* [2003].
[b]Combined estimate based on work by *Jochum et al.* [1983], *Salters and Stracke* [2004], and *Workman and Hart* [2005].

MORB source mantle, and the continental crust has been considered to be internally inconsistent. This is usually interpreted as an argument for the existence of a hidden mantle reservoir storing a significant amount of K, U, and Th [e.g., *Kellogg et al.* 1999]. One of the formulations of Earth's HPE budget is the following. Earth's current heat flux is currently ~44 TW [*Pollack et al.*, 1993]. This flux is made of contributions from Earth's secular cooling and from the radioactive decay of the heat-producing elements. The model of the primitive mantle composition by *McDonough and Sun* [1995] results in radiogenic heat production in the bulk silicate Earth at ~20 TW. Of this, ~8 TW constitutes the heat flux originating in radiogenic isotopes in continental crust (using the crustal compositional model by *Rudnick and Gao* [2003]). Therefore ~12 TW should be coming from the radioactive decay in Earth' mantle. The MORB source mantle is, however, highly depleted in incompatible elements. If the depleted mantle constitutes the entire mantle, its heat production would be 3–5 TW (based on the compositional model for the MORB source mantle [e.g., *Salters and Stracke*, 2004; *Workman and Hart*, 2005]). Therefore a complementary reservoir with HPE producing up to 9 TW of heat should be hidden somewhere in the mantle.

[30] Earth's thermal budget therefore seems to provide a strong argument for layered convection. However, if we consider uncertainties associated with estimates for the HPE content in the bulk Earth as well as the continental crust and the depleted mantle, the discrepancy between heat production in the bulk silicate Earth and its reservoirs diminishes considerably. Errors for the HPE abundance in the bulk silicate Earth are roughly estimated to be 15–20% by *McDonough and Sun* [1995], which result in the range of 16–24 TW for the BSE heat flux. The compositional model of the continental crust by *Rudnick and Gao* [2003] is characterized by at least 30% uncertainty for the crustal HPE abundance, which results in 5–10 TW of heat flux. Therefore the amount of the heat flux coming from the mantle should be within 6–19 TW. The lower bound of this estimate is close to the depleted mantle heat production of 3–5 TW. Moreover, a slightly enriched model for the MORB source mantle suggested by *Jochum et al.* [1983] and *Korenaga* [2006] (with 100 ppm K, 8 ppb U and 16 ppb Th) results in ~6 TW. Given these uncertainties, the global budget of HPE does not appear as a strong argument for a hidden reservoir even with existing compositional models, though we are certainly pushing ourselves to the edge of confidence limit.

[31] Our PM composition model is noticeably depleted in HPEs compared to the conventional model of *McDonough and Sun* [1995]. Table 2 compares the estimates of HPE budgets according to these two models. The HPE amount in the new BSE model is in general agreement with the combined budget of continental crust and the MORB source mantle. The corresponding estimate for radiogenic heat flow from the bulk silicate Earth is 13–19 TW, which overlaps with the range of 8–15 TW originating in the continental crust [e.g., *Rudnick and Gao* 2003] and the depleted mantle [e.g., *Salters and Stracke*, 2004; *Workman and Hart*, 2005]. Thus there is no need to postulate the existence of a large-scale hidden reservoir enriched in HPEs.

3.2. Thermal Evolution Models

[32] Apart from the geochemical context discussed in section 3.1, Earth's budget of heat-producing elements has frequently been considered from the geodynamical point of view as well. As Earth's internal heat is an important energy source for mantle convection, modeling the thermal evolution of Earth heavily relies on the budget of heat-producing elements, and by the same token, thermal evolution models have often been used to infer the geodynamically preferred amount of internal heat production. Many previous arguments around this coupled thermal budget and evolution are, however, confusing and sometimes simply incorrect. Here we point to common misconceptions and explain why our revised thermal budget makes sense both in the geodynamical and geochemical contexts.

[33] A key parameter for thermal evolution is the Urey ratio, Ur, which measures the contribution of internal heating to the total convective heat flux. When $Ur = 0$, there is no internal heating in the system, and when $Ur = 1$, all convective heat flux is balanced by internal heat production. We note that not all of existing literature follow this definition of the Urey ratio. For example, it is common in geochemical literature that the Urey ratio is taken as the contribution of all of internal heating with respect to all of surface heat flux. With the present-day terrestrial heat flux of ~44 TW [*Pollack et al.*, 1993] therefore a conventional value of BSE heat production (~20 TW [*McDonough and*

Sun, 1995]) may appear to correspond to the Urey ratio of ~0.5. This definition of the Urey ratio is, however, not the same as that adopted in thermal evolution models. As thermal evolution is modeled based on the theory of convection, what matters is the contribution of heat production in convecting mantle to heat released by mantle convection. As radiogenic heat production in the continental crust is ~8 TW, this conductive heat flux must be subtracted from both internal heat production and surface heat flux. Dividing ~12 TW by ~36 TW, we thus obtain the Urey ratio of ~0.3. Taking into account the uncertainties of heat production in the continental crust (5–10 TW) and in the BSE (13–19 TW, based on our new composition model), the range of the plausible Urey ratio is 0.09–0.36. The uncertainty of the total heat flux itself is not considered here because it is estimated to be small (1–2 TW) according to *Pollack et al.* [1993]. The dominant part of terrestrial heat flux is carried by oceanic heat flow, which is tightly constrained by the well-defined depth-age relationship, and it is unlikely to have errors larger than a few TW.

[34] By assuming that the MORB source mantle occupies the entire mantle, we can also estimate heat production in convecting mantle directly from its composition. As mentioned earlier, this hypothetical mantle would produce 3–5 TW according to the composition model of *Salters and Stracke* [2004]. With convective heat flux of 34–39 TW, this heat production would correspond to the Urey ratio of 0.08–0.15. Though this range certainly belongs to the lower end of the Urey ratio based on the BSE model, it is nonetheless within the uncertainty. This is not surprising because this exercise is merely to rephrase the global budget of heat-producing elements in terms of the Urey ratio. Again, we emphasize that the petrologically observed mantle (through mid-ocean ridge magmatism) is sufficient to explain the global thermal budget. Geochemical inference does not impose us the existence of a hidden HPE-enriched reservoir, if the limitation of our knowledge is properly recognized.

[35] This geochemical estimate of the Urey ratio, whether it is 0.3 or 0.15, has often been regarded to be too low to explain the long-term thermal history of Earth. A usual line of logic is the following. The Urey ratio of 0.3, for example, means that the 70% of convective heat flux is due to secular cooling, which in turn indicates that Earth must have been very hot in the past. The rate of secular cooling is, on the other hand, constrained to be not greater than 80 K Gyr^{-1}, based on the petrogenesis of Archean and Proterozoic igneous rocks [*Abbott et al.*, 1994; *Grove and Parman*, 2004]. A number of similar parameterized convection models have been studied to quantify secular cooling [e.g., *Schubert et al.*, 1980; *Richter*, 1984; *Christensen*, 1985], and most models indicate that the Urey ratio must be as high as 0.7 to prevent a catastrophic thermal history, if whole mantle convection is assumed. The assumption of whole mantle convection and the use of the high Urey ratio, however, are hard to reconcile with the depleted nature of the petrologically observed mantle. The Urey ratio for the MORB source mantle is 0.15 at most, so one must face a difficult task to explain how the whole mantle can be 5 times more enriched in HPE without showing such indication in the global mid-ocean ridge system.

[36] Though some researchers take this inconsistency in these whole mantle evolution models as a supporting fact for layered convection [e.g., *Kellogg et al.*, 1999], others have looked into a more fundamental issue regarding the modeling of thermal history itself. *Christensen* [1985] was the first to propose that the classical theory of thermal convection might not be appropriate to model the thermal evolution of Earth. A catastrophic thermal history indicated by a low Urey ratio essentially results from the assumption that hotter mantle convects faster and thus releases greater heat. A high degree of secular cooling dictated by a low Urey ratio implies hotter mantle and thus higher heat flux, and because internal heating can vary only slowly owing to the long half-lives of radiogenic isotopes, this higher heat flux results in an even lower Urey ratio, thereby completing a positive feedback. Though Christensen's original argument was later pointed out to be invalid [e.g., *Gurnis*, 1989; *Solomatov*, 1995], more recent studies on the energetics of plate tectonic convection [*Korenaga*, 2003, 2006] suggest that hotter mantle in the past may have convected slower and thus released less heat than present-day.

[37] Mantle viscosity is highly spatially variable because of its dependence on temperature, pressure, stress, grain size, and composition, and a critical issue is which part of the mantle controls the speed of convection. Plate tectonics is a unique convective phenomenon on Earth, in which the cold and strong boundary layer completely recycles back to the interior. Considerable energy dissipation is thus expected when this boundary layer is deformed at subduction zones [*Solomatov*, 1995; *Conrad and Hager*, 1999]. *Korenaga* [2003] pointed out that the thickness of the boundary layer can substantially be affected by mantle melting beneath mid-ocean ridges because of dehydration stiffening [*Karato*, 1986; *Hirth and Kohlstedt*, 1996]. Hotter mantle in the past most likely started to melt deeper, creating thicker, compositionally stiffened lithosphere. The deformation of this thick lithosphere at subduction zones could be an important bottleneck of plate tectonic convection. A self-consistent calculation based on boundary layer theory suggests that it is likely to have more sluggish plate tectonics in the past, and this theoretical prediction appears to be supported by the history of continental aggregation for the last 3 Ga, in two different ways: (1) the inferred rate of global plate motion and (2) the subductability of oceanic lithosphere (see *Korenaga* [2006] for details). On the basis of this new energetics of plate tectonic convection, *Korenaga* [2006] demonstrated that one can reconstruct a geologically reasonable thermal history with the Urey ratio of 0.15–0.30 in the framework of simple whole mantle convection. This long-term thermal evolution of Earth is consistent with our thermal budget and also with the assumption of global-scale mantle homogeneity.

3.3. Th/U Systematics

[38] Thorium-uranium systematics offers a slightly different perspective on this heat budget issue. *Turcotte et al.* [2001] argue that the MORB source mantle with Th/U ratio (κ) ~2.5 [e.g., *Bourdon et al.*, 1996] and the continental crust with κ < 6.0 [e.g., *McLennan and Taylor* 1980] together cannot account for the bulk silicate Earth Th/U ratio, which is relatively well established at 3.8–4.0 based on measurements in carbonaceous chondrites [e.g., *Rocholl*

and Jochum, 1993] and Pb isotope evolution [e.g., *Allègre et al.*, 1986]. Their mass balance calculation appears to imply that a complementary reservoir with κ of 4.0 comprising about half of the mantle is required to compensate the low Th/U of the MORB source, but as we will demonstrate below, their argument is misleading.

[39] Readers are referred to *Turcotte et al.* [2001] for the details of theoretical formulation, and only a brief outline is given here. They divide the silicate Earth into three reservoirs, the upper (depleted) mantle, the lower (primitive) mantle, and the continental crust. The mass fraction of the upper mantle is denoted by m. If there is no hidden reservoir, for example, we have $m = 1$. The lower mantle is assumed to have the bulk earth Th/U as well as BSE U concentration (C_{UBSE}). The primary unknowns in their mass balance are C_{UC} (U concentration in the continental crust), C_{UUM} (U concentration in the upper mantle), C_{UBSE} (note: they denote this as C_{ULM}), and κ_{C} (Th/U ratio in the continental crust). They derived two mass balance constraints and two heat flow constraints, and when other parameters like m and Ur are fixed, we can uniquely determine these four unknowns. We follow their formulation almost exactly; only differences are that the convective heat flux and the radiogenic heat production in continental crust are set to 36 TW and 8 TW, respectively (as discussed previously), and that we tested different values of K/U (10000 and 12700) and the bulk Earth Th/U (3.8 and 4.0). These differences do not affect the main conclusion of *Turcotte et al.* [2001]. Our results are summarized in Figure 2.

[40] The essence of the argument by *Turcotte et al.* [2001] is the following. By looking at how κ_{C} varies with a given Ur (Figure 2a), the fraction of the upper mantle m should be smaller than $\sim$0.5 in order to keep $\kappa_{\mathrm{C}} < 6.0$. One may note that such conclusion may not be valid if Ur can be sufficiently low. For example, even the extreme case of $m = 1$ cannot be rejected if $Ur \sim 0.2$. *Turcotte et al.* [2001, p. 4270] rejected this possibility and restricted their attention to the cases of $Ur > 0.5$, by stating

> Many authors have utilized convection calculations to establish values for the Urey number.... Values for the Urey number using this approach are generally in the range $Ur = 0.6-0.8$. *Richter* [1984] showed that layered-mantle convection favors a higher value. *Christensen* [1985] found $Ur \approx 0.5$ by utilizing a viscous rheology for the lithosphere, but this approach has not been generally accepted. The preferred parameterized convection solutions require concentrations of heat-producing elements that are 50–100% higher than those given by geochemical considerations.

[41] As emphasized in section 3.2, however, such high Urey ratios assumed in a number of previous whole mantle parameterized convection models are in direct conflict with petrological observations. Also, the work of *Richter* [1984] is miscited in the above. *Richter* [1984] discounted the notion of whole mantle convection because it requires a high Urey ratio inconsistent with geochemistry, and he turned to layered-mantle convection in order to satisfy geochemical considerations. In light of the energetics of plate tectonic convection [*Korenaga*, 2006], their argument for high Urey ratios is now unfounded, and the geodynamically preferred Urey ratio is finally consistent with geochemical considerations, being in the range of 0.15–0.30.

[42] With this proper understanding of the Urey ratio, the Th/U systematics is consistent with the global-scale homogeneity, i.e., $m \approx 1$, in every aspect of this mass balance. For $Ur = 0.15-0.30$ (as indicated by our new BSE model, Figure 2d) and $m \approx 1$, the κ_{C} constraint is satisfied (Figure 2a), C_{UUM} is consistent with the estimate of *Salters and Stracke* [2004] (Figure 2b), and C_{UC} agrees with the estimate of *Rudnick and Gao* [2003] (Figure 2c).

3.4. Helium and Heat Flux Imbalance

[43] *O'Nions and Oxburgh* [1983] were the first to examine Earth's helium flux in comparison with heat production. They concluded that the amount of U and Th in the mantle required to support the oceanic radiogenic ^{4}He flux would only provide $\sim$5% of the mantle heat flux. This result is generally interpreted as an argument for the two-layered mantle, with the convecting upper mantle that loses its small amount of radiogenic heat and helium efficiently, and the isolated lower mantle that emanates heat but traps the noble gases [e.g., *O'Nions and Oxburgh*, 1983; *Allègre*, 2002].

[44] The calculation by *O'Nions and Oxburgh* [1983] is, however, based on the assumption that the oceanic heat flux originates entirely from the radioactive decay of HPE. The secular cooling component is thus totally neglected. As was shown in sections 3.1–3.3, however, our best estimate for the Urey ratio (0.15–0.3) indicates that secular cooling is an essential part of Earth's heat budget, and may comprise more than 70% of the global heat flow. Moreover, the steady state assumption used by *O'Nions and Oxburgh* [1983] and also in more resent studies [e.g., *O'Nions and Tolstikhin*, 1996; *Schubert et al.*, 2001] is likely to be inappropriate when trying to model the release of noble gases from the mantle. Because only partially molten mantle processed at the mid-ocean ridges is being degassed, the rate of degassing is not necessarily equal to the rate of production. In the following we will show that the rate of mantle processing at the mid-ocean ridges and the present-day fluxes of ^{4}He are consistent with the global-scale homogeneity of Earth's mantle.

[45] ^{4}He is produced by the decay of the following three radioactive nuclides: ^{238}U ($\rightarrow$ ^{206}Pb + 8 ^{4}He), ^{235}U ($\rightarrow$ ^{207}Pb + 7 ^{4}He), and ^{232}Th ($\rightarrow$ ^{206}Pb + 6 ^{4}He). The molar flux of ^{4}He produced by U and Th in Earth's mantle can thus be expressed in terms of mantle U concentration and Th/U ratio:

$$f_{^4He} = MC_U\left(\frac{8\ \%_{238}\lambda_{238}}{238} + \frac{7\ \%_{235}\lambda_{235}}{235} + \frac{6\lambda_{232}}{232}\frac{C_{Th}}{C_U}\right), \qquad (1)$$

where λ_{238}, λ_{235}, and λ_{232} are the decay constants of ^{238}U, ^{235}U, and ^{232}Th nuclides; $\%_{238} = 0.99275$ and $\%_{235} = 0.0072$ are natural occurrences of ^{238}U and ^{235}U; C_U and C_{Th} are mantle concentrations of U and Th, and M is the mass of mantle that is being degassed.

[46] In previous works equation (1) has been used to derive the estimate of the U concentration in Earth's mantle based on the observed ^{4}He flux [*O'Nions and Oxburgh*, 1983], or to determine the ^{4}He flux corresponding to the assumed U content in the mantle [*Schubert et al.*, 2001]. The calculations have been based on the steady state assumption, i.e., the mass of the entire mantle has been

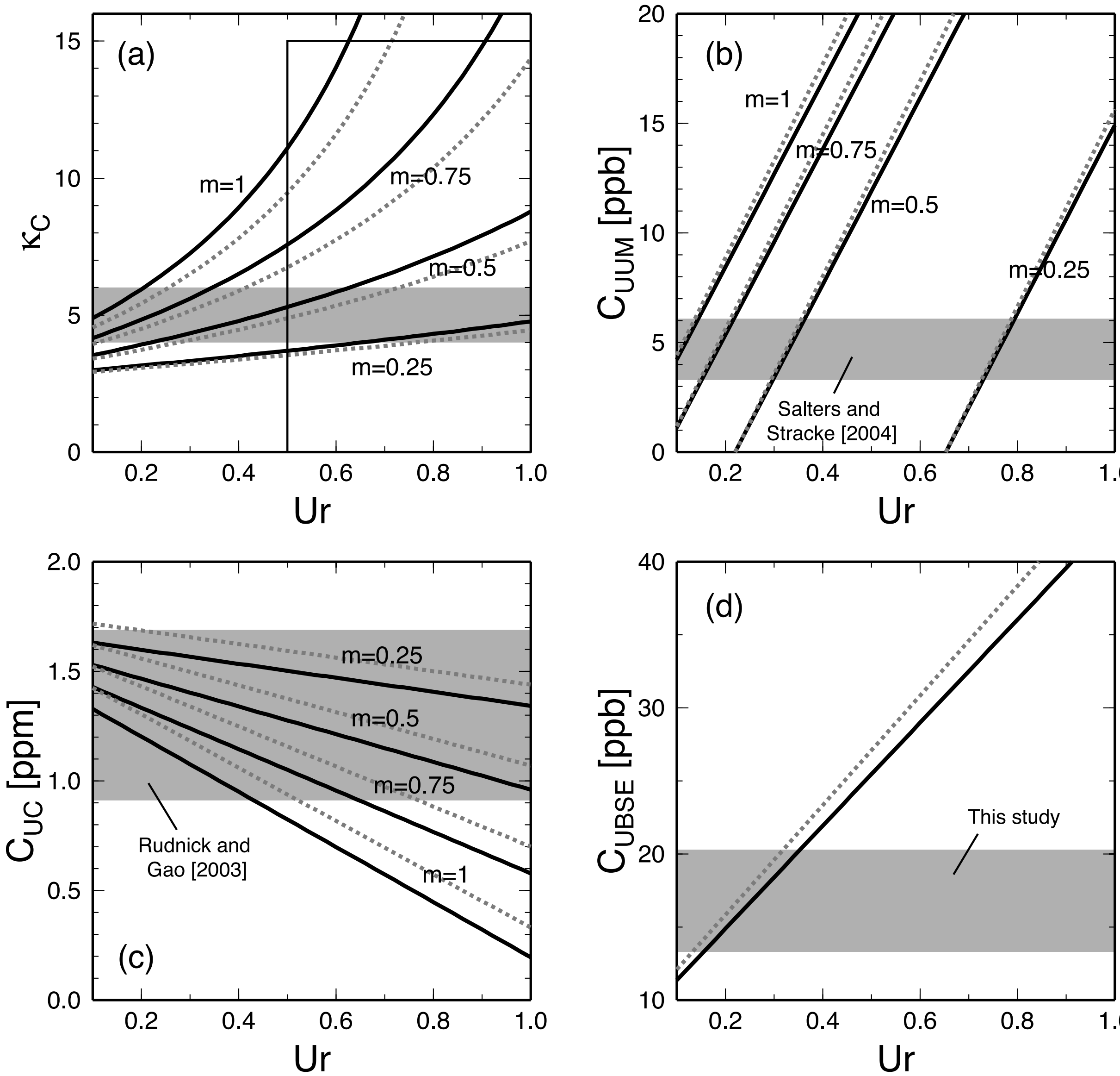

Figure 2. Solutions (as a function of *Ur*) for Th/U systematics formulated by *Turcotte et al.* [2001]. The κ_{UM} is fixed at 2.5. Solid curves are for κ_{BSE} of 4.0 and K/U of 12,700, and dotted curves for κ_{BSE} of 3.8 and K/U of 10,000. Cases for four different *m* values (0.25, 0.5, 0.75, and 1.0) are shown. (a) Th/U ratio in continental crust. Gray shading indicates the range of acceptable κ_{C}. The rectangular region corresponds to the range of Figure 4 of *Turcotte et al.* [2001]. (b) U concentration in depleted upper mantle. Gray shading is based on the estimate by *Salters and Stracke* [2004]. (c) U concentration in continental crust. Gray shading is based on the estimate by *Rudnick and Gao* [2003]. (d) U concentration in BSE. Gray shading is based on our new model. Note that C_{UBSE} does not depend on the value of *m*.

used for *M*. In both cases, the large discrepancy between the observed values and those derived from equation (1) leads to the conclusion that the present-day mantle ^{4}He flux is much lower than that expected from the estimated HPE content of the mantle.

[47] As noble gases are released from partially molten mantle beneath mid-ocean ridges, in our calculation we will use $M = R_{proc}\, t$, where R_{proc} is the rate of mantle processing at mid-ocean ridges, 5.76×10^{14} g yr^{-1}, and *t* is time. We further assume that the MORB source mantle with C_U = 4.7 ± 1.4 ppb and C_{Th} = 13.7 ± 4.1 ppb [*Salters and Stracke*, 2004] constitutes the entire mantle. This depleted mantle is assumed to have been almost entirely degassed some time early in Earth's history, and since then ^{4}He has been produced by the decay of U and Th and stored in the mantle until released at present-day mid-ocean ridges. The time of this initial outgassing is then given by *t*. We can derive our estimate for *t* based on the observed ^{4}He flux at mid-ocean ridges, $f_{^4He}$ ~9.8×10^7 mol yr^{-1} (section 2.3). If this calculation results in a very small value of *t*, then the

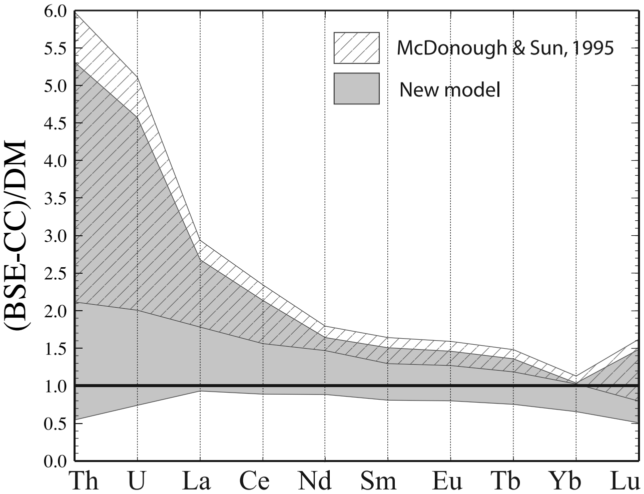

Figure 3. Global mass balance of refractory lithophile elements. The vertical axes represents the ratio of the present-day mantle composition (i.e., the BSE minus the continental crust), to the MORB source mantle composition by *Salters and Stracke* [2004]. Elements are plotted in order of increasing compatibility. Continental crust composition is from *Rudnick and Gao* [2003]; the uncertainty is estimated at ~50% for La and ~30% for other elements, based on the comparison with other crustal models (see discussion by *Rudnick and Gao* [2003, and references therein]). Unity corresponds to the present-day mantle entirely composed of the MORB source mantle, i.e., BSE − CC = DM. See text for detailed discussion.

observed helium flux is too low given the HPE content of the MORB source. On the contrary, unrealistically large t would indicate that the amount of HPE in the depleted mantle cannot support the observed flux of helium. Our estimate for t, based on the above values for helium flux and MORB source composition, is 4.0 ± 1.2 Ga, which agrees well with accepted scenarios of Earth's evolution [*Halliday*, 2003]. The large uncertainty of the t estimate comes from ~30% error in the He flux [*Craig et al.*, 1975]. Taking into account the uncertainties in the MORB source composition will result in even wider range of t, (4.0 ± 3.0 Ga). Similar calculation could in principle be performed using the observed molar flux of ^{40}Ar. The ^{40}Ar flux from the mantle is unfortunately very poorly constrained (see section 2.3 for detailed discussion), and the corresponding values for t range between 1 Ga to at least 30 Ga.

[48] If we assume the entire mantle is composed of the depleted mantle (i.e., 4.7 ppb U and 13.7 ppb Th), the present-day production rate of ^{4}He in the mantle is $\sim 16 \times 10^7$ mol yr^{-1}. Observed degassing rate of 9.8×10^7 mol yr^{-1}, so the efficiency of degassing is ~60%. The numerical modeling on helium degassing from convecting mantle [*van Keken et al.*, 2001] shows a similar degree of efficiency (~75%), suggesting that the steady state assumption is unlikely to be valid. However, we note that the work of *van Keken et al.* [2001] is misleading in one critical aspect. For the sake of simplicity, they ignored the extraction of continental crust when they modeled mantle convection for the duration of 4 Gyr, and thus their model mantle is highly enriched in heat-producing elements (with the present-day concentration of 20 ppb U and 76 ppb Th). The production rate of ^{4}He in their present-day mantle is thus very high (87×10^7 mol yr^{-1}), and so is the average degassing rate (66×10^7 mol yr^{-1}). They compared this degassing rate with the observed degassing rate (9.8×10^7 mol yr^{-1}), and concluded that the argument of *O'Nions and Oxburgh* [1983] is still robust. This conclusion is simply due to their use of the PM composition for the present-day mantle. If we scale down their numerical results by using the estimate of *Salters and Stracke* [2004], their numerical study would instead invalidate the argument of *O'Nions and Oxburgh* [1983].

[49] To sum, helium is not as efficiently extracted as heat, because the degassing of helium is limited to where mantle is processed by magmatism. On the other hand, heat can be extracted everywhere on Earth's surface by thermal conduction. There is no reason to expect a balance between these two completely different physical processes to begin with. The amount of helium in the mantle could increase with time, and as we did in the above, we can use the observed helium flux to estimate the timescale of mantle processing (~4 Gyr), which is exactly what the new thermal evolution model predicts [*Korenaga*, 2006]. The helium and heat flux "imbalance" problem is an artifact, originating in the neglect of secular cooling by *O'Nions and Oxburgh* [1983], which has never been completely corrected in subsequent studies.

4. Mass Balance of Lithophile Elements

[50] The mass balance of lithophile elements, most frequently the rare earth elements, thorium, and uranium, has often been used to argue for the existence of mantle heterogeneity [*Helffrich and Wood*, 2001; it *Albaréde and van der Hilst*, 2002]. As lithophile elements do not enter the core, they must be distributed among different reservoirs in the silicate Earth. Similar to the budget of heat-producing elements discussed in section 3.1, the rare earth content of the bulk silicate Earth, based on the conventional BSE model by *McDonough and Sun* [1995], does not match the combined budget of the crust and the depleted mantle. This is conventionally interpreted as an argument for the existence of a mantle reservoir enriched in these incompatible elements.

[51] Mass balance calculations based on our new compositional model of the BSE along with the model for the continental crust [*Rudnick and Gao*, 2003] eliminate this inconsistency. One way to demonstrate it is to compare our estimate for the composition of the present-day mantle (i.e., bulk silicate Earth minus continental crust composition) with recent estimates for the MORB source mantle composition. In Figure 3 we show an example of such comparison with *Salters and Stracke* [2004] model for the MORB source mantle. Although uncertainties associated with this type of calculation are fairly large, as they include all the uncertainties of the BSE, continental crust (CC) and depleted mantle (DM) models, it is evident that the present-day mantle composition based on the standard BSE model [*McDonough and Sun*, 1995] is considerably more enriched in Th, U and rare earth elements compared to the MORB source mantle. By contrast, our new BSE model is consistent with the present-day mantle entirely composed of the

MORB source mantle, though there might be a relatively small-scale heterogeneity in Earth's mantle enriched in highly incompatible elements as suggested by a trend in Figure 3.

[52] We note that this mass balance calculation is still preliminary, because the DM model by *Salters and Stracke* [2004] (or *Workman and Hart* [2005]) is partly based on the BSE model by *McDonough and Sun* [1995]. Recently, however, *Langmuir et al.* [2005] proposed a new composition model for the "interactive" mantle (i.e., the global average of mantle sources that are sampled by mid-ocean ridges), which is entirely independent of any BSE model. Their model is actually more enriched in highly incompatible elements than previous DM models, and when combined with our BSE model, it completely eliminates a need for a hidden reservoir (C. H. Langmuir, personal communication, 2006).

5. Discussion and Conclusions

5.1. The ^{142}Nd Mantle Heterogeneity

[53] The new high-precision isotopic measurements of meteorites showed that most of the chondrites have consistently lower ^{142}Nd/^{144}Nd ratios compared to the terrestrial standard [*Boyet and Carlson*, 2005]. Chondrites have always been used as reference when reconstructing isotopic evolution of Earth, as these primitive meteorites are expected to represent the "building blocks" of Earth's accretion. The discrepancy between the chondritic and the terrestrial ^{142}Nd/^{144}Nd standards implies that all known terrestrial rocks derive from a mantle reservoir with a higher-than-chondritic Sm/Nd ratio. Therefore the silicate Earth that is available for observations should have diverted from the evolution of the chondritic uniform reservoir (CHUR) some time early in its history.

[54] The higher-than-chondritic Sm/Nd ratio in Earth's mantle may be explained by (1) early global differentiation event that divided the primitive silicate Earth with the chondritic Sm/Nd ratio into a high Sm/Nd reservoir, from which all the known terrestrial rocks derived, and a complementary (hidden) low Sm/Nd reservoir, or (2) the nonchondritic composition of Earth's building blocks.

[55] The first explanation, which is favored by *Boyet and Carlson* [2005], implies the existence of a mantle reservoir that has never been sampled and thus should have remained isolated from mantle convection for Earth's entire history. The size of this reservoir depends on its (unknown) Sm/Nd ratio, and thus cannot be constrained. Mass balance considerations, however, require this reservoir to be fairly small (perhaps less than 5% of the mantle volume [*Boyet and Carlson*, 2005]); otherwise, the extraction of continental crust would result in higher ^{143}Nd/^{144}Nd ratios for MORBs than observed. Therefore the possibility of ^{142}Nd heterogeneity does not require the isolation of a large fraction of mantle, being consistent with whole mantle convection model. The most important implication of this global early differentiation model is, however, a nonprimitive source for the continental crust, which contradicts the common view that the continental crust and the complementary MORB source mantle are the melt and the residue of the primitive mantle [e.g., *Hofmann*, 1988, 2003]. The early global differentiation scenario would thus require revision of the existing models of continental crust extraction and mantle evolution.

[56] The alternative explanation, i.e., a slightly nonchondritic composition for BSE, is not so radical as it may sound. In the early differentiation scenario, the suggested timing of deviation from the CHUR evolution is perhaps less than 30 Myr and not later than 100 Myr from the beginning of the solar system [*Boyet and Carlson*, 2005]. We first note that this timing is comparable with the timescale of Earth's accretion. Combined constraints imposed by tungsten and lead isotope data suggest that the time required to accumulate 63% of Earth's mass with exponentially decreasing accretion rates, must lie in the range of 10–20 Myr [e.g., *Halliday*, 2003]. The addition of material to Earth by giant impacts and heavy bombardment lasted until at least ~100 Myr after the start of the solar system [e.g., *Halliday*, 2000, 2003]. Second, the ratios of refractory elements, Sm, Nd, U, Th, etc., are only approximately constant among different kinds of chondrites, and they still exhibit noticeable variability. Figure 4 shows the variations of Sm/Nd, Ca/Al, and Ti/Sm, among different chondritic groups. Even within the carbonaceous class of chondrites (one that is most often associated with Earth's building material, [e.g., *Allègre et al.*, 2001]), Sm/Nd ratio varies by as much as 10%.

[57] For this reason, it is not easy to define an accurate chondritic reference value for Earth's refractory ratios. As CI carbonaceous chondrite is the most primitive among other chondrites and its composition most closely resembles the composition of the solar photosphere [*Palme and O'Neill*, 2003], the common practice is to use CI refractory ratios as reference values for Earth [e.g., *McDonough and Sun*, 1995]. On the other hand, when defining the isotopic reference for Earth, *Jacobsen and Wasserburg* [1980] selected ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd ratios close to the values for the C2 and C3 carbonaceous chondrites, Murchison and Allende, as it appears impossible to uniquely determine an initial isotopic composition for the solar system from the range of compositions present in chondrites. The present-day accepted isotope reference value of ^{147}Sm/^{144}Nd, 0.1966 [*Jacobsen and Wasserburg*, 1980; *Dickin*, 2005], thus corresponds to elemental ratio Sm/Nd ~0.3121, which is ~4% lower than the CI and the solar Sm/Nd ~0.3260. Therefore, even if the primordial material that accreted to build Earth had refractory ratios, and particularly the Sm/Nd ratio, within the chondritic range, there is a nontrivial uncertainty about the exact values of those ratios. Moreover, accretion process itself might have affected the composition of the growing Earth. Primitive planetesimals have probably differentiated extremely quickly due to the heat from runaway growth and the decay of live ^{26}Al [*Chambers*, 2003]. As Sm and Nd have different compatibilities in silicate melt, igneous differentiation should have fractionated the Sm/Nd ratio, resulting in low Sm/Nd in the outer portions of planetesimal bodies. Impact erosion might be expected to preferentially remove major portions of the outer silicate portions of accreting planetesimals [*Halliday*, 2003]. The result would be a slightly elevated Sm/Nd ratio in the growing Earth.

[58] A slightly elevated Sm/Nd ratio corresponds to a more radiogenic ^{143}Nd/^{144}Nd ratio, and the bulk silicate earth having ε^{143}Nd of up to ~4 is actually permissible,

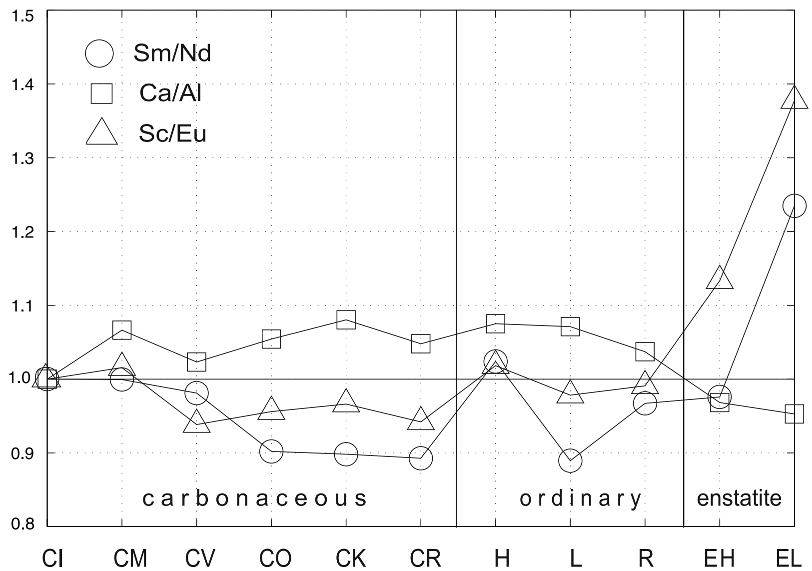

Figure 4. Variation of some lithophile refractory ratios among different chondritic groups, based on the compilation by *Lodders and Fegley* [1998]. Average compositions of all chondritic groups are normalized by CI composition.

because the ε^{143}Nd of the depleted mantle was already as high as ~4 at the beginning of the existing record (~4 Ga) [e.g., *Bennett*, 2003]. This possibility could potentially undermine global mass balance calculations based on ε^{143}Nd [e.g., *Jacobsen and Wasserburg*, 1979; *DePaolo*, 1980; *Lassiter*, 2004].

[59] Regardless of whether the deviation of silicate Earth from the CHUR $\varepsilon_{143_{Nd}}$ evolution is explained by global differentiation event, or a not exactly chondritic Sm/Nd ratio in the bulk silicate Earth, ^{142}Nd heterogeneity does not contradict the whole mantle convection model. Note that a 5–10% higher ^{147}Sm/^{144}Nd ratio in the bulk silicate Earth compared to the initial chondritic ^{147}Sm/^{144}Nd of 0.1966 (equivalent to elemental Sm/Nd 0.3121), would not disagree with the new BSE model proposed in our companion paper, because in our inversion method we allow up to ~5% deviations from the CI reference value for elemental Sm/Nd ratio of 0.3260 [*McDonough and Sun*, 1995; *Lodders and Fegley*, 1998].

5.2. Seismic Heterogeneity

[60] As shear (S) and compressional (P) wave velocities have different sensitivities to temperature and mineral composition, seismic data can be used to infer the compositional structure of Earth's mantle. In particular, a positive correlation between S and P wave velocity perturbations is consistent with a thermal origin of seismic anomaly, whereas their anticorrelation suggests chemical heterogeneity or the presence of volatiles [e.g., *Stacey*, 1998]. Seismic velocities can reflect the change in major element composition, i.e., Mg, Si and Fe content [*Bina*, 2003] but are insensitive to trace element composition. However, in order to maintain layered-mantle convection, there should exist a sufficient density contrast between two layers, which implies major element heterogeneity.

[61] In recent years there have been a number of seismological studies that reported possible compositional heterogeneity in the mantle below ~1100 km depth [e.g., *Robertson and Woodhouse*, 1996; *Su and Dziewonski*, 1997; *van der Hilst and Kárason*, 1999; *Trampert et al.*, 2004]. Many tomographic models show that perturbations in bulk sound speed negatively correlate with perturbations in shear velocity in at least part of the lower mantle (e.g., see the review by *Masters et al.* [2000, and references therein]). The ratio of relative variations in shear versus compressional wave speed, $R = d \ln V_S/d \ln V_P$, is usually used as a diagnostic of the physical cause of an anomaly. Theoretical works on the properties of lower mantle phases show that a value of $R \leq 2.5$ in the lower mantle is compatible with pressure and thermal effects, whereas higher R implies the existence of compositional heterogeneity [e.g., *Isaak et al.*, 1992; *Karato and Karki*, 2001]. Although different tomographic models yield slightly different results, a conservative estimate for the spherically averaged R profile presented by *Masters et al.* [2000] seems to be consistent with the one predicted for purely thermal effects [*Karato and Karki*, 2001]. Note that *Karato and Karki* [2001] refer to the R estimate based on constrained inversion by *Masters et al.* [2000]; this R profile indicates chemical heterogeneity at the lowermost mantle. *Masters et al.* [2000], however, favor more general, unconstrained inversion, which results in an R profile that does not require any chemical zoning throughout the mantle, in light of the mineral physics prediction by *Karato and Karki* [2001]. Negative correlations between shear and bulk wave velocities in the lower mantle should thus originate from lateral variations in bulk chemical composition of the mantle (e.g., caused by subducted oceanic lithosphere [*Saltzer et al.*, 2001]), rather than vertical stratification in chemical composition. Good agreement between calculated lower mantle velocities for a number of candidate compositions of oceanic lithosphere and the observed P and S wave velocity heterogeneities also supports the model of subducted slabs

as a source for seismic heterogeneity [see *Bina*, 2003, and references therein].

[62] The interpretation of seismic data in terms of density is complicated and sometimes controversial. In particular, although the free oscillation (normal mode) data and the free-air gravity anomaly data have been used to infer a noticeable high-density anomaly in the lower mantle beneath the Pacific Ocean and Africa [*Ishii and Tromp*, 1999], later works showed that density structure cannot be reliably resolved based on normal mode data [*Resovsky and Ritzwoller*, 1999; *Masters et al.*, 2000; *Romanowicz*, 2001; *Kuo and Romanowicz*, 2002]. Nonetheless, some tomographic models [e.g., *Ni et al.*, 2002; *Trampert et al.*, 2004] identified seismic anomalies under Pacific and Africa as dense and having chemical origin. Piles of subducted crust, chemical interaction with the core, or partial melting are often mentioned as possible causes for those anomalies, [e.g., *Masters et al.*, 2000; *Bréger and Romanowicz*, 2001]. Still, because the horizontally averaged *R* profile does not contradict the one predicted for thermal effects only [*Karato and Karki*, 2001], and the radial density profile does not indicate noticeable density stratification on a global scale [*Masters and Gubbins*, 2003], the existence of those anomalies may be consistent with radially homogeneous mantle, in which lateral composition and density variations are introduced by subducting slabs and maintained by inefficient mixing.

5.3. Summary: "Low-CaRb" Marble-Cake Mantle

[63] The new compositional model for the primitive mantle proposed in our companion paper is noticeably depleted in a number of refractory (e.g., Ca, Al, REE, U, Th) and nonrefractory (e.g., Rb, K, Cs, Pb) elements, compared to the commonly accepted model by *McDonough and Sun* [1995]. Similar to previous models [e.g., *Hart and Zindler*, 1986; *McDonough and Sun*, 1995; *Palme and O'Neill*, 2003], our model is based on the upper mantle peridotite compositions, thus requiring an assumption about large-scale mantle homogeneity in order to account for the composition of the entire mantle. Although this assumption was regarded debatable due to a number of inconsistencies in mass balance calculations based on the previous BSE models [*McDonough and Sun*, 1995; *Palme and Jones*, 2003], our revised global budget of noble gases and trace elements, including heat-producing elements, supports the view of mantle homogeneity on a global scale. Figure 1 presents our conceptual model of Earth's mantle based on the new BSE composition. The present-day mantle is almost entirely composed of the MORB source mantle, as indicated by mass balance calculations. The uncertainty of global mass balance is such that the presence of small-scale mantle heterogeneities is likely. This model is thus analogous to the so-called "marble-cake" model [e.g., *Allègre and Turcotte*, 1986], or the "blob" model [e.g., *Helffrich and Wood*, 2001], but is depleted in a number of refractory as well as nonrefractory elements.

[64] The most likely candidate for the source of small-scale mantle heterogeneities is subducted oceanic lithosphere. Anomalies in seismic wave velocity and scattering of seismic energy in the lower mantle [e.g., *van der Hilst and Kárason*, 1999; *Masters et al.*, 2000; *Saltzer et al.*, 2001] suggest the existence of lateral variations in the bulk mantle composition, whereas horizontally averaged mantle structure inferred from seismic data does not indicate compositional layering [e.g., *Masters et al.*, 2000; *Karato and Karki*, 2001]. Globally homogeneous mantle containing the remnants of subducted slabs at different depths is consistent with these observations. The distinct geochemical signature of OIB can also be explained by subducted oceanic lithosphere of various ages [e.g., *Hauri and Hart*, 1993; *Lassiter and Hauri*, 1998], as well as by differences in mantle flow and lithospheric thickness between mid-ocean ridges and hot spots [e.g., *Ito and Mahoney*, 2005].

[65] The preservation of small-scale chemical heterogeneity and primordial signatures in MORB and OIB mantle sources, despite convecting stirring, can be explained by inefficient mixing in Earth's mantle. A recent work on thermal evolution by *Korenaga* [2006] suggests that contrary to the common belief, plate tectonics might have been more sluggish in the past. Sluggish mantle convection is required to explain Earth's thermal budget as well as petrological data on the degree of secular cooling in the past (see section 3.2). Sluggish mantle convection may explain the presence of long-lived mantle heterogeneities and inefficient noble gas degassing in the context of whole mantle convection, since the estimated time for processing the entire mantle through mid-ocean ridges would be as long as ~4 Gyr [*Korenaga*, 2006]. The emerging model of Earth's mantle, largely of MORB source composition, with small-scale geochemical heterogeneities originating in subducted oceanic lithosphere of different ages, is thus entirely self-consistent, and agrees well with available geochemical and geodynamical constraints.

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