Major and trace element composition of the depleted MORB mantle (DMM)

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Received 4 May 2004; received in revised form 1 December 2004; accepted 8 December 2004
Available online 20 January 2005
Editor: R.D. van der Hilst

Abstract

We derive an estimate for the chemical composition of the depleted MORB mantle (DMM), the source reservoir to mid-ocean ridge basalts (MORBs), which represents at least 30% the mass of the whole silicate Earth. A database for the chemical and physical properties of abyssal peridotites has become robust and complete enough to truly access a reference DMM. Using trace element depletion trends from the abyssal peridotites, it is possible to construct a large part of DMM's trace element pattern. Splicing this information with isotopic constraints (Sr–Nd–Pb–Hf) and canonical ratios (Ce/Pb, Nb/Ta, Nb/U, Ba/Rb, H2O/Ce, CO2/Nb and Cl/K), we can extend abundance estimates to all the incompatible elements including volatile content. The resulting trace element pattern for average DMM constrains parental MORB to be generated by 6% aggregated fractional melting, consistent with recent models for hydrous melting of the mantle [P.D. Asimow, J.E. Dixon, C.H. Langmuir, A hydrous melting and fractionation model for mid-ocean ridge basalts: application to the Mid-Atlantic Ridge near the Azores, Geochem. Geophys. Geosyst. 5 (2004) 10.1029/2003GC000568]. We show that DMM is roughly balanced by the continental crust and better balanced upon inclusion of ocean island basalt source and oceanic crust components. Compared to the primitive mantle, DMM has been depleted by 2–3% melt extraction and has only 15% the radiogenic heat production.

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Keywords: DMM; major elements; trace elements; mid-ocean ridge basalts; mantle

1. Introduction

The trace element composition of the depleted upper mantle (DMM) is a fundamental parameter in modeling the generation of mid-ocean ridge basalts (MORBs), calculating the crust–mantle mass balance, and establishing the chemical and thermal evolution of the Earth. To date, all attempts to establish an average composition for the upper mantle, whether by parent/daughter derivations from isotopic systems [1–6] or by MORB trace element inversions [6–9], have centered on MORB liquids and included major
assumptions about melt generation, melt transport, and differentiation processes that have affected these upper mantle melts. Unfortunately, it is just these processes that we are trying to understand, rather than assume a priori.

The most compelling evidence for upper mantle depletion comes from the heavy-element isotopic composition of MORBs. Although MORBs and their residues, abyssal peridotites, have some degree of heterogeneity in radiogenic isotope ratios (Sr–Nd–Pb–Hf), they are focused within a small range of values relative to ocean island basalts and are, with very few exceptions, depleted from bulk earth values in $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{176}\text{Hf}/^{177}\text{Hf}$, thus requiring a long-term history of low Rb/Sr, Hf/Lu, and Nd/Sm (i.e. incompatible element depletion). Direct evidence for upper mantle depletion came with the classic trace element studies of Johnson et al. [10] and Johnson and Dick [11] on abyssal peridotites, but most of the observed depletion in these peridotites is due to melt extraction during the latest spreading events, so that the composition of the general ambient upper mantle has been severely overprinted by this latest melting episode.

Ultimately, we know that this mantle, which has been estimated to comprise 30–70% by mass of the bulk silicate earth, has been depleted over time in the highly incompatible (lithophile) elements ([1,8], refs. therein). Most models ascribe the depletion of the upper mantle to the extraction of the enriched continental crust, a process that has removed up to 90% of the most incompatible elements, and 80–85% of the heat-producing elements (e.g. [8]). Some part of the depletion may also be created by the preservation of recycled oceanic crust that is currently sequestered in unknown regions of the mantle. It is possible the lower mantle (below 670 km) has also been depleted by such processes, but this question is highly controversial at present.

In place of assuming a set of bulk partition coefficients or a degree of melt extraction, we use in this paper the following constraints in deriving an average trace element composition of DMM: (1) trace element content of clinopyroxenes from abyssal peridotites, (2) isotopic evolution from primitive upper mantle (PUM), and (3) canonical trace element ratios in MORBs. Abyssal peridotite data from the literature, the backbone of this study, are treated in a way reminiscent of studies such as Loubet et al. [12], Hart and Zindler [13], and McDonough and Sun [14]. Abyssal peridotites, unlike basalts, are not modified by secondary processes such as fractional crystallization, magma mixing, and crustal assimilation [15], but may be subject to melt impregnation [16] and melt/rock reaction [17]. We show that melt impregnation can be recognized and therefore filtered from the abyssal peridotite data set and suggest that melt/rock reaction in the data set we have used has had more effect on major element chemistry than trace element chemistry. Overall, it seems that, for the moderately incompatible elements, abyssal peridotites more accurately record the trend of upper mantle depletion than do MORBs.

The average trace element content of DMM, as deduced here, generally shows a very smooth pattern with increasing trace element compatibility, which to first order mass-balances with the continental crust. The degree of depletion indicated in DMM represents 2–3% melt removal from the primitive upper mantle (PUM) of McDonough and Sun [14]; this means that DMM has only 15% the radiogenic heat production of PUM (from K, U, and Th). Present-day ocean crust (i.e. MORBs) can be modeled with 6% aggregated fractional melting of the deduced DMM.

2. Trace element composition of DMM

2.1. Abyssal peridotites

Abyssal peridotites have been shown to be residues of fractional or near-fractional melting that produces MORB (e.g. [10]). Although bulk trace element compositions of these peridotites are heavily modified by alteration on the seafloor, many workers have analyzed the trace element compositions (Sr, Zr, Ti, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Y) of relict, unaltered clinopyroxene grains as a means of chemical characterization [10,11,18–21]. Using such clinopyroxene compositions, bulk compositions ($C_{\text{WholeRock}}$) of the peridotites can be calculated for each trace element with the following equation:

$$C_{\text{WholeRock}} = C_{\text{cpx}} \left( \frac{D_{\text{bulk}}}{D_{\text{cpx}}} \right)$$

Where the bulk partition coefficient ($D_{\text{bulk}}$) is determined from modal abundances ($x_{\text{mineral}}$) of olivine (ol), orthopyroxene (opx), clinopyroxene (cpx), and spinel.
(sp), and mineral/melt partition coefficients ($D_{\text{mineral}}$) as follows:

$$D_{\text{bulk}} = x_{\text{ol}} D_{\text{ol}} + x_{\text{opx}} D_{\text{opx}} + x_{\text{cpx}} D_{\text{cpx}} + x_{\text{sp}} D_{\text{sp}}$$ (2)

This method of calculating bulk peridotite compositions is a substitute for a more accurate method, which would be to sum the concentrations of trace elements in minerals according to their modal proportions. Converting to whole rock compositions from clinopyroxene alone is done simply due to the fact that almost no trace element data exist for other minerals in the peridotite samples.

We have compiled a data set from the literature that includes abyssal peridotites having both cpx trace element analyses and modal abundances (data sources are [10,11,15,18–21]). All samples containing more than 1% modal plagioclase are excluded on the basis that most plagioclase in abyssal peridotites has been interpreted as a secondary phase representative of melt impregnation [16,21]; as a result, only 5 out of almost 90 samples included have any reported modal plagioclase at all. Anomalously high Ce and Sr values have also been excluded for some samples. For Sr, some anomalous values are suspected seawater alteration; such Sr anomalies are not accompanied by Eu anomalies and therefore are not suspected to be plagioclase reaction products. For both Sr and Ce, the most incompatible elements of the sample suite and therefore the most depleted in abyssal peridotites, elevated concentrations are probably due to small amounts of melt impregnation (see discussion below).

The final trace element data set for the abyssal peridotites, corrected to whole rock compositions using mineral/melt partition coefficients from Kelemen et al. [22], published modal abundances and the above equations, is shown in Fig. 1 and can be obtained in Appendix A. It is important to note that the geographical distribution of the sample suite is highly focused on the Southern Ocean; 90% of the samples originate from the American–Antarctic, Southwest Indian and Central Indian Mid-Ocean Ridges, with the remaining 10% obtained from the Mid-Atlantic Ridge and East Pacific Rise. The question of whether or not this geographical bias manifests as a chemical bias will not be answered until larger data sets from other localities are established.

The purpose of compiling bulk rock information is to derive the inter-relationships between different trace elements (i.e. to what degree the various incompatible

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Fig. 1. Calculated whole rock trace element compositions of abyssal peridotites. Data can be found in Appendix A; data sources as quoted in the text.
trace elements are depleted relative to each other over the entire history of mantle depletion). A formulation of the trace element “system” begins by interpreting the trace element compositions of peridotites using the equation for a residue of fractional melting (see Zou [23] for review of melting models). Calculations show that modal fractional melting used to interpret residues of melting is a fine approximation for any number of more complicated melting models (see Appendix A).

The ratio of the concentration of a given element in a solid, $C_s$, to its original concentration, $C_o$, after some fraction of melting, $F$, is as follows:

$$
\frac{C_s}{C_o} = (1 - F)^{(\frac{1}{D} - 1)} 
$$

(3)

Where $D$ is the bulk solid/melt partition coefficient for modal melting.

The relationship between the concentrations of two elements in the residue, $[A]$ and $[B]$, can be linearized upon equating two equations solved for $F$:

$$
\ln \left( \frac{C^A_s}{C^B_o} \right) = R \ln \left( \frac{C^A_o}{C^B_o} \right) + \ln \left( \frac{C^A_o}{C^B_o} \right) 
$$

(4)

Where the slope, $R$, on the linear ln([A]) vs. ln([B]) array is a function of the bulk partition coefficients for elements $A$ and $B$:

$$
R = \frac{D_B(1 - D_A)}{D_A(1 - D_B)} 
$$

(5)

Given that we have information for 12 different elements (see Fig. 1), there are 132 of the ln([A]) vs. ln([B]) relationships to consider in the overall reduction of this data set; Fig. 2 shows a sampling of these linear arrays, with the more incompatible of a given element pair plotted on the x-axis. The peridotites show an extremely wide range in degree of depletion and form well-correlated depletion trends for upper mantle melting. Correlations are best for those element pairs having similar bulk $D$ values (see the Sm–Nd, Sm–Eu and Dy–Er panels in Fig. 2), and fall off slightly for elements with increasingly dissimilar bulk $D$’s (see Zr–Ti and Sm–Yb). Some of the scatter in correlations may have been produced by melt impregnation. For instance, impregnation of low degree melts into highly depleted residues would cause points to fall off the depletion trends toward the more incompatible element, as shown in Fig. 2. Melt impregnation trajectories for relationships among the HREE (e.g. Dy–Er) very closely overlap their well-correlated arrays (not shown for clarity), thereby indicating that melt impregnation has none to very little effect on the slopes or positions of these depletion trends.

The ln([A]) vs. ln([B]) depletion trends have been fit by a York [24] two-error regression (Fig. 2), assuming a blanket error of 10% for all points. The regressions have also been forced through the primitive upper mantle (PUM) coordinate of McDonough and Sun [14]; most regressions intersect the PUM coordinate without forcing, but this treatment becomes appropriate for some regressions with poor correlations (for example, see the Ce–Nd panel in Fig. 2) and we find it necessary for obtaining robust output from the regression scheme.

The upper mantle is certainly not a unique composition (isotopic or otherwise), but rather a range of compositions reflecting variable amounts of depletion and/or re-enrichment. A given peridotite’s bulk trace element composition represents the culmination of melt depletion and enrichment over the entire history of that peridotite. Also, integrated within the trace element trends (Fig. 2) is the net transfer of material out of the mantle by oceanic and continental crust generation as well as crustal recycling, in so far as the recycled material is well mixed within the upper mantle. In this sense, some of the more complicated processes affecting upper mantle composition are incorporated into the abyssal peridotite trends, but are not required to explain the trace element data.

Knowing that much of the depletion observed in abyssal peridotites is caused by the most recent melting event, we need to define where today’s average, unmelted upper mantle lies on the depletion trends. For this we need another constraint, the most obvious being the isotopic evolution of DMM: calculating the present-day Sm/Nd ratio from $^{143}$Nd/$^{144}$Nd signatures in MORBs defines a unique position on the abyssal peridotite depletion trends.

2.2. Isotope constraints

Although there has been much written on the homogeneity of MORBs relative to OIBs [25–27], it is clear from the global database (Fig. 3) that the
MORB mantle is not one sole isotopic composition and by inference not one sole trace element composition. The variation in MORB $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ compared to all oceanic basalts is 18%, 35%, and 47%, respectively. To address this issue of compositional heterogeneity in the upper mantle we derive three different trace element compositions for the MORB source by calculating present-day parent/daughter ratios from isotopic signatures and relating those ratios to the abyssal peridotite depletion trends. A study by Su and Langmuir [28], who have filtered global MORB data for proximity to subduction zones and known plumes/hot spots (Fig. 3; Table 1), provides an average MORB isotopic composition ($\text{Sr–Nd–Pb}$) as well as a standard deviation of the isotope data. We use the Su and Langmuir [28] data analysis to define the following: (1) the average DMM composition, (2) an E-DMM based on isotopes that are $2\sigma$ enriched over the average, and (3) a D-DMM based on isotopes

Fig. 2. Co-variation diagrams for trace elements in abyssal peridotites, plotted as $\ln([A])$ against $\ln([B])$ in accordance with Eq. (4); the more incompatible element is on the x-axis for each plot. Star symbol is Primitive Upper Mantle (PUM; also Bulk Silicate Earth, BSE) of McDonough and Sun [14]. Solid line is the best-fit regression, forced through the PUM coordinate and with assigned errors of 10% for each point. The curved lines with crosses (in the middle three panels) are trajectories for impregnation of a 1% melt of DMM (see Fig. 7; $D$ values from Kelemen et al. [22]) into a depleted mantle of composition indicated by the points of origin on the regression lines; ticks are in increments of 0.1% up to a total of 1% melt impregnation.
that are 2σ depleted from the average. The
\(^{176}\text{Hf}/^{177}\text{Hf}\) value of DMM is selected by averaging MORB values from Nowell et al. [29], Chauvel and Blichert-Toft [30], and Andres et al. [31]; \(^{176}\text{Hf}/^{177}\text{Hf}\) values for E-DMM and D-DMM are based on correlations with \(^{143}\text{Nd}/^{144}\text{Nd}\) (e.g. [30]).

To derive present-day parent/daughter ratios, a depletion model must be assumed. It is common to use a two-stage evolution model with a single, instantaneous depletion event at a time \((t)\) equal to the average age of the continental crust. An example from the Rb–Sr system, where \(T\) is the age of the Earth and parent/daughter ratios are for present-day is the following:

\[
\frac{\text{\(^{87}\text{Sr}/^{86}\text{Sr}\) DMM}}{\text{\(^{87}\text{Sr}/^{86}\text{Sr}\) BSE}} = \left(\frac{\text{\(^{87}\text{Rb}/^{86}\text{Sr}\) DMM}}{\text{e}^{\lambda T}} - 1\right) + \left(\frac{\text{\(^{87}\text{Rb}/^{86}\text{Sr}\) BSE}}{\text{e}^{\lambda t}} - 1\right)
\]

(6)

However, because mantle depletion is largely the result of continental crust extraction, it is important to consider continental growth through time and the fact that it is not a single depletion event as modeled in the above equation. Although there is debate about continuous growth [32] or constant volume with crustal recycling [33–35], somewhere in between (such as episodic growth) is probably the reality [36–38]. Models suggesting continuous growth generally agree that the real increase in continental mass was at about 3 Ga [37]. Models in favor of constant crustal volume suggest rapid (or at least effective) recycling of crust.
greater than 3 billion years old (e.g. [34,39]). For our
purpose, it is really preservation that is of issue; even
though there are isotopic arguments for a 4.0 Ga
depleted mantle of similar size and degree of depletion
as the modern depleted mantle (e.g. [39,40]), it is more
important here that the abundance of that old crust is
low compared to crust younger than 3.0 Ga. Isotopi-
cally, the recycling of old crust would make depletion
appear to be younger on average and smear out (or even
negate) the signal of ancient depletion.

Here we have improved on the classical methods
by using a continuous transport, melt depletion model
starting at 3 Ga. The equation for the Sr isotopic
composition of DMM at time, \( t \), as derived by Alle`gre
[41] and Hart and Brooks [42] is:

\[
\frac{^{87}\text{Sr}}{^{86}\text{Sr}}_t = \frac{^{87}\text{Sr}}{^{86}\text{Sr}}_o + \frac{\lambda(\frac{^{87}\text{Rb}}{^{86}\text{Sr}})_o [1 - e^{-(\lambda + k)t}]}{\lambda + k}
\]

where \( \lambda \) is the decay constant for \(^{87}\text{Rb} \) and \( k \) is the
difference in transport coefficients between Rb and Sr
and essentially relates to the difference between bulk
partitioning of the two elements. The initial conditions
are values for bulk silicate Earth at the time when
deployment begins (3.0 Ga). The parameter, \( k \), is solved
for by knowing the isotopic composition of bulk Earth
at 3 Ga and DMM at time zero (i.e. present-day), as
shown in Table 1. The parent/daughter variation
through time is then:

\[
\left( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_t = \left( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_o e^{-(\lambda + k)t}
\]

Fig. 4 shows how this model, as used for the Rb/Sr
system, gives a factor of ~2 lower estimate for the
present-day Rb/Sr ratio of DMM, compared to the
usual two-stage model. Decreasing the age of depletion
requires lower Rb/Sr ratios for the same present-day
\(^{87}\text{Sr} / ^{86}\text{Sr} \) ratio. In the same way that the Sr isotopes are
used to constrain the Rb/Sr ratio of DMM, similar
constraints result in determinations for Sm/Nd, Lu/Hf,
and U/Pb (Table 1). The choice of depletion model does
not greatly affect the Sm–Nd system, but is important
for the whole suite of parent/daughter ratios.

Fig. 4. Plot showing examples of instantaneous depletion and continuous depletion models for the isotopic evolution of Sr in DMM. Note that
the derived Rb/Sr ratio of today’s upper mantle varies by a factor of about two between the models—the Rb/Sr ratio is defined by the slope of
the evolution curves. Nd isotopic evolution by continuous depletion is not shown since it is essentially linear through time. See Table 1 for
isotope evolution parameters and Eqs. (7) and (8) for continuous depletion model.
Most important to the abyssal peridotite inversion is the present-day Sm/Nd ratio for DMM, since this identifies the present-day position of DMM on the mantle depletion arrays. Fig. 5 shows how the Sm/Nd ratio of 0.411 in average DMM has a unique intersection with the Sm–Nd abyssal peridotite regression line, defining unique Sm and Nd concentrations of 0.239 ppm and 0.581 ppm, respectively. Given the absolute concentrations of Sm and Nd, we can derive the absolute concentrations of all the other trace elements that have been analyzed in abyssal peridotites (REE, Sr, Zr, Ti, Y; Table 2). Ultimately, estimates for every element concentration are obtained based on relationships with every other element. Standard deviations of various estimates for a given element are on the order of 1–2% for REE’s and Ti and 5–6% for Sr, Zr, and Ce, indicating that the depletion trends are internally very consistent; note that these standard deviations do not testify to the accuracy of the model. With other parent/daughter ratios, other pieces of the trace element pattern for DMM are estimated: Rb derives directly from the Sr; Hf derives from extrapolation to Lu from the REE’s; Pb derives from the Ce/Pb canonical ratio (see below); and U follows (Table 2). The same procedure is applied with the E-DMM and D-DMM isotopic compositions.

It is possible to derive Th concentrations from Th/U ratios inferred from 208Pb/204Pb and 206Pb/204Pb isotopic evolution. However, it has been widely recognized that inferred Th/U ratios are generally much higher than observed Th/U ratios in MORBs; this has been termed the ‘kappa conundrum’ [2,5,43]. Since Th and U are both highly incompatible during mantle melting, with Th being slightly more incompatible, the Th/U ratios of MORBs should provide an upper limit to the source Th/U. Due to the extremely long half-life of 232Th (14 Byr), we interpret the kappa conundrum to be a problem where the Th–Pb system has not “caught-up” with the U–Pb system. For a more accurate representation of present-day upper mantle, we use Th/U ratios measured by careful U-Series studies on MORBs [44–46] over the range in isotopic composition used to define our D-DMM through to E-DMM (Table 1).

2.3. Canonical ratios and volatile contents

There are few trace element ratios in MORBs (as well as many OIBs) that remain constant over variable degree of melting and variable isotopic composition. These ratios (Ce/Pb, Nb/Ta, Nb/U, and Ba/Rb) are termed “canonical” and their constancy is interpreted to be due to bulk partition coefficients being very nearly the same for the element pairs during upper mantle melting, preventing significant fractionation [47–52]. Hence, ratios in the melts are presumed to be identical to ratios of these elements in the source.

We employ these canonical ratios in order to complete the trace element pattern of DMM. It is clear though, from Fig. 6, that some canonical ratios are better behaved than others; Nb/Ta, Nb/U, and Ba/Rb all hover about their published values of 15.5, 47, and 11.3, respectively [47–49,51,52], whereas Ce/Pb ratios display much more scatter with a significant distribution of data higher than either published canonical values of 25 and 20 [48,50]. As a mid-value of the MORB data, we use a Ce/Pb ratio of 30; if, in studies to come, it is determined that Ce/Pb should be lower, we recommend changing only the Pb concentration in
DMM, as the U–Nb–Ta–La–Ce segment of the trace element patterns derived is consistent with MORB trace element characteristics (see Section 3.2). This would imply that the derived U/Pb ratios from Pb isotopic inversions are not accurate—i.e. that U and Pb cycling in the upper mantle is more complicated than is assumed to be here. All other canonical ratios used are as previously published.

There is also a suite of canonical ratios involving the volatile elements H, C, and Cl that are useful for estimating the budget of these elements in the upper mantle. Volatile elements play an important role in melt generation and transport, so the following estimates are crucial input parameters for modeling such processes. The compatibility of water has been shown to be similar to that of Ce, and MORBs have on average an H2O/Ce ratio of ~200 [53]. Using Ce=0.550 ppm (Table 2), H2O is calculated to be 110 ppm in DMM. Using a lower limit of 150 and upper limit of 250 for H2O/Ce [53] along with our lower and upper estimates for Ce (Table 2), respectively, the range of water content in DMM is 70–160 ppm.

In a recent study on volatile undersaturated basaltic melt inclusions from the Siqueiros transform fault, Saal [54] have established two new working canonical ratios: CO2/Nb at 239\textsuperscript{\textcircled{F}}46 and Cl/K at 0.0075\textsuperscript{\textcircled{F}}0.0025. Using our Nb min/max estimates from Table 2 and our K estimate from Table 3 (see Section 3.1 below), average DMM has a CO2 content of 36\textpm42 ppm and a Cl content of 0.38\textpm0.25 ppm. These estimates are about

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<th>Table 2 Trace element composition of DMM</th>
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\textsuperscript{a} Normalized to primitive upper mantle (PUM) with values from McDonough and Sun [14].

\textsuperscript{b} Minimum and maximum estimates for average DMM concentrations, based on assuming initiation of continuous depletion at 2.5 Ga and 3.5 Ga, respectively.

\textsuperscript{c} Bulk partition coefficients calculated from Eq.(5), assuming $D_{\text{Nd}}=0.031$ and solving for all other $D$’s; 1\sigma errors (%) are based on the variation of $D$ estimates obtained from various regressions involving a given element. Values in italics are from Kelemen et al. [22], except Rb, which is assumed, and U and Th, which are based on our own literature compilation. Underlined values are interpolated between regression outputs.
2 times lower than those reported by Saal et al. [54] due to their use of different trace element abundances in DMM, but within error of recent estimates by Salters and Stracke [6].

2.4. Final product

Combining the mantle depletion trends from the abyssal peridotites, parent/daughter ratios from the isotopic evolution of DMM, and a handful of canonical ratios, trace element patterns (“spidergrams”) of average DMM, E-DMM (enriched from the average), and D-DMM (depleted from the average) have been derived (Fig. 7a; Table 1 for isotope values; Table 2 for trace element compositions). Overall, the spidergrams are very smooth except for a dip in Sr along with an expected Pb anomaly (see Hofmann, [8]). The greatest difference between the three compositions is in the highly incompatible elements; for example, Rb and Ba vary by a factor of ~5, but Sm varies by only 30%.

Because it is difficult to assign errors to the estimated compositions, we have provided minimum and maximum estimates for trace element concentrations in the average DMM by using starting ages for the continuous depletion model at 2.5 and 3.5 Ga, respectively (see the grey lines on Fig. 7b; Table 2). By changing the initial assumption of depletion age, we are effectively saying DMM is more or less depleted and all elements together move up or down the depletion arrays in proportion to their compatibilities during melting. Each of these patterns is internally consistent, and therefore not a true range for each element but rather a coherent solution for the assumptions made. It is not advisable to “mix and match” values from different patterns, since the elements behave as a system, not independently, and should be regarded as such. However, the Ba/Th ratios...
for the 2.5 and 3.5 Ga patterns are, respectively, too high and too low to generate realistic MORB compositions (see Section 3.2) and support the idea that 3.0 Ga is an appropriate assumption for initiation of mantle depletion. As an aside, using a classical 1.8 Ga instantaneous depletion model results in a spidergram (not shown) very similar to that of the 3.5 Ga pattern but with Rb and Ba close to values for the 3.0 Ga (preferred) pattern.

The Salters and Stracke [6] spidergram (Fig. 7b) for average DMM, based on depleted MORB elemental ratios and isotopic evolution, is generally less depleted than the average DMM of this study. In particular, they show significantly higher estimates for the whole left side of the spidergram (Rb to Ce), as well as higher Zr, Hf and Y, than predicted even for our maximum estimate; this is most likely due to their use of an instantaneous (two-stage) depletion model for isotopic evolution instead of the gradual depletion model described in this paper.

Please note that in the following sections, only average DMM is discussed.

3. Physical and chemical properties of DMM

3.1. Modal abundances and major elements

Abyssal peridotites from all over the world show depletion trends not only in trace element content, but also in major element content in the form of modal abundances and mineral compositions [15,18,19,55–57]. In general, these observations are supported by experimental and theoretical studies of peridotite melting [58–61]. With increasing degree of melt
depletion, olivine increases in modal proportion while orthopyroxene, clinopyroxene, and spinel decrease. Al, Ca, Na, K, and Ti are more incompatible during melting than Mg, Cr, and Ni, so have the highest mineral and whole rock concentrations in the least depleted peridotites (e.g. [57]).
Since we have established the systematics of incompatible trace elements in abyssal peridotites (see above), we use their relationship to modes to estimate the proportion of minerals in today’s average DMM, then challenge the results with considerations of melt extraction and a comparison to the primitive mantle. Using the same data set as employed earlier (obtainable from Appendix A), we have plotted bulk trace element concentrations against modal abundances in individual abyssal peridotites (see examples in Fig. 8); note that these are not completely independent parameters since modes in part determine bulk trace element contents. By extrapolating the trends like those in Fig. 8 to the DMM trace element concentrations (Table 2), we find DMM to be composed of 57% ol, 28% opx, 13% cpx, and 2% sp (Table 3); orthopyroxene does not correlate with any trace elements and has been solved for by summation to 100%. These modes are very close to those found by extrapolating the modal abundance correlations for the South–West Indian Ridge abyssal peridotites [16] for which, without spinel, yields 60% ol, 30% opx, and 10% cpx.

Constructing the bulk depleted mantle composition from mineral modes requires fairly precise knowledge of oxide abundances in the mantle minerals. Baker and Beckett [57] have reduced mineral data for abyssal peridotites and provided algorithms for estimating major element compositions of minerals according to the modal abundance of olivine. Using the Baker and Beckett [57] mineral compositions at 57% olivine and combining the minerals in the given proportions, results in a bulk DMM having an Al$_2$O$_3$ content nearly that of the primitive upper mantle (PUM; McDonough and Sun [14]), along with a very low Ca/Al ratio compared to PUM. Since Al is depleted during melt extraction and Al is more enriched than Ca in mantle melts (see Table 3), it is reasonable to expect the depleted mantle to have lower Ca and Al concentrations and an equal or higher Ca/Al ratio than that of PUM. This seems to be a problem only with Al abundance and is interpreted to be due to extrapolating mineral compositions beyond the limit of data used by Baker and Beckett [57]. For this reason, we find it more appropriate to use mineral compositions at 60% olivine, the lowermost (i.e. fertile) limit of their regressed data. In doing so, we calculate the major element composition of DMM as reported in Table 3.

Compared to PUM, estimated DMM has, as expected, lower SiO$_2$, TiO$_2$, Al$_2$O$_3$, CaO, Na$_2$O, and K$_2$O with higher MgO and Cr$_2$O$_3$ (Table 3). The TiO$_2$ content of 0.13 wt.% is very close to the 0.12 wt.% calculated from the trace element derivation (Table 2). The CaO/Al$_2$O$_3$ ratio is equal to that of PUM (0.80), and would increase to 0.86 by lowering the spinel abundance by only 0.5%. As previously mentioned, much of the trace element depletion in the upper mantle can be attributed to the continental crust. The question now is: can the newly
estimated major element depletion also be attributed to the continental crust? The continental crust budget (see mass-balance section below and bulk continental crust of Rudnick and Fountain [62]) does largely account for the low TiO₂ and K₂O, the most incompatible of the major elements, and partially accounts for the Na₂O. However, owing to the small mass of continental crust, major elements with less contrast between the crust and mantle cannot be balanced solely by the continents. As a possible solution, Table 3 shows a rudimentary mass balance of the DMM major elements in which 3% of primary MORB is subtracted from PUM (note that this is not a melting model). The major elements calculated in this way show striking similarity to the estimated DMM composition, implying that there is an isolated reservoir of oceanic crust somewhere within the silicate Earth, as also suggested by Hauri and Hart [63]. A second estimate for Na₂O based on mass balance with both the continental crust and a MORB reservoir is also provided in Table 3 and is most likely more accurate than the original sum of mineral compositions.

To convert mineral modes into practical information for those who study abyssal peridotites, we have calculated the trace element composition of the constituent minerals in unmelted, average DMM by using Eqs. (1) and (2) with mineral/melt partition coefficients compiled by Kelemen et al. [22]. This effectively distributes the DMM trace element budget among the minerals according to their relative affinity for incompatible elements. The resulting mineral compositions can be found in Appendix A.

As a cautionary note, the reported modes and mineral compositions will only apply to the very shallow mantle, owing to variable mineral compositions and phases with pressure and temperature, but the average bulk composition of unmelted, upper mantle should be similar at any depth in this reservoir.

### 3.2. MORB generation

Here we present the average DMM trace element composition, so should be able to produce an average parental N-MORB. To model MORB generation, we first calculate bulk partition coefficients \( D \) from Eq. (5) applied to the abyssal peridotite depletion trends. Because the slopes of the depletion trends (Fig. 2) only supply information about ratios of \( D \) values, we initially have to assume a \( D \) for one element and then calculate the remainder in relation to that one. We have chosen a bulk \( D_{Nd} \) of 0.031, according to a compilation from Kelemen et al. [22] for upper mantle melting, since the bulk compatibility of Nd is almost identical in both the spinel and garnet facies.

The set of partition coefficients resulting from the inversion of all abyssal peridotite depletion trends is reported in Table 2. Fig. 9 shows the calculated \( D \) values compared to both garnet and spinel facies bulk \( D \)’s from Kelemen et al. [22]; clearly the slope of the calculated \( D \) values very closely matches that of spinel facies melting and is far off the slope of garnet facies melting. Note that choosing a different \( D_{Nd} \) will change the absolute position but not the slope of the \( D \) values shown in Fig. 9 (meaning the ratios of \( D \)’s will not change). The above observation does not exclude a contribution of trace elements from small degree melts in the garnet facies, especially for elements with low \( D \) values; this may be why Sr and Ce are a little lower than the spinel facies prediction. For elements with higher bulk \( D \)’s in the garnet facies, the majority of depletion will happen in the spinel facies, thus is reflected in the depletion arrays. If depletion for the middle to heavy REE’s was significant in garnet melting, the trace element pattern across the REE would be steeper, even if the last \( D \) values to act on the peridotites were those of spinel melting. This is a straightforward effect of fractional melting on residues.

As an average MORB trace element pattern to be fit by our modeling, we use the parental (fractionation-corrected) N-MORB reported by Su and Langmuir [28]. A point generally agreed upon, and hence applied here, is that MORBs are aggregated fractional or near-fractional melts over a range of pressures, as initially confirmed by Sobolev and Shimizu [64]. The highly incompatible elements are enriched ~16-fold over DMM, thus requiring 6% aggregated fractional melting of DMM. Fig. 10 shows the excellent fit to N-MORB using the \( D \) values derived here and reported in Table 2.

The 6% degree of melting to generate MORB is on the low side of previous estimates ranging from 6–20% [65,66]. A higher \( F \) could be obtained if a greater fractionation correction is applied to the already-corrected parental N-MORB of Su and Langmuir [28] since \( F \) is mainly limited by the concentration of highly incompatible elements (i.e. Rb, Ba, U, Th, Nb,
Fig. 9. Bulk partition coefficients ($D$’s) as obtained from abyssal peridotite trends (Fig. 2; Table 2) plotted against both spinel and garnet facies bulk $D$ values from Kelemen et al. [22]. Regression-based $D$ values are calculated with Eq. (5) and assuming $D_{\text{Nd}}=0.031$. It is clear that the slope of the $D$ values obtained reflect melting more in the spinel facies than the garnet facies, as the garnet facies is much steeper. Another choice for $D_{\text{Nd}}$ will change the absolute values, but not the slope, of the points plotted here.

Fig. 10. Plot showing the spectacular fit of parental N-MORB (from Su and Langmuir [28]) by 6% aggregated fractional melting of DMM (from this study) using bulk $D$ values in Table 2. The Rb, Ba, Th, U, and Pb for the parental MORB are taken from the N-MORB average of Hofmann [8] and adjusted according to fractionation corrections provided by Su and Langmuir [28].
Ta in the modeled MORB; however, this requires generally higher $D$’s to maintain the proper slope for M- to HREE. To get to $F = 10\%$, at least another 30\% fractionation is necessary and this seems unlikely. This low value for $F$, as compared to previous models, may be due to the fact that older estimates are based on anhydrous melting. Water content in the upper mantle is increasingly recognized as a very important aspect of mantle viscosity and convection [67] as well and mantle melting [68–71]. To test the validity of 6\% mean $F$, we apply our estimated concentration of H$_2$O to the recent model by Asimow et al. [70] for hydrous mantle melting (the pHMELTS model).

A pHMELTS model run, using 110 ppm water, the major element compositions in Table 3, a potential temperature of 1360 °C, a 2-D passive triangle melting regime, and near-fractional melting, results in 7.0\% mean melting to produce MORB and a crustal thickness of 6.3 km (P. Asimow, pers. comm., 2004). This confirms that the mean degree of melting (as defined by Plank et al. [72]) for hydrous models is generally on the low side of previous estimates from anhydrous models.

For average DMM, the derived $D$ values (Table 2) translate into 2–3\% melt depletion from primitive mantle using either non-modal or modal fractional melting models. Because average DMM is only 2–3\% melt depleted, but average MORB is generated by 6\% melting, one or all of the following is implied: (1) the degree of melting was lower in the past, (2) the mantle is a cannibal, recycling some crust and lithosphere back into itself, (3) depleted mantle has exchanged with the less depleted mantle, or (4) MORB generation is not the process that depletes the mantle.

4. Crust–mantle mass balance

Classic works based on continental crust and the depleted mantle being sole complementaries calculate that from 30\% to 70\% of the mantle is depleted according to isotope and parent/daughter constraints ([1], refs. therein). In the following paragraphs, we provide three different scenarios for the balance of chemical reservoirs in the silicate earth, with each scenario progressively involving additional reservoirs. We believe that using the entire trace element suite to assess the extent to which the silicate earth does or does not mass-balance is a robust way to calculate relative proportions of reservoirs. The mass of the continental crust is fixed to be 0.6\% the mass of the silicate Earth. For each scenario, the best estimates of reservoir masses along with uncertainty in the estimates are derived from a Monte Carlo simulation with $10^5$ trials in which element concentrations for each reservoir are considered as normal random variables with means given as PUM normalized concentrations and 1σ equal to 10\%; in each trial, the relative reservoir masses are determined by a linear least-squares fit to the input parameters. Uncertainties are quoted as 2σ.

Scenario 1 is our own mass-balance involving only DMM and the continental crust, meaning in what proportion do DMM and the continental crust have to be added in order to sum back to primitive mantle? Our calculations indicate that 33±3\% of the mass of the silicate Earth has to be DMM, with the remainder being primitive mantle, to best balance the bulk continental crust composition as estimated by Rudnick and Fountain [62]. For this particular ‘reconstituted’ mantle, all elements sum to within 15\% of the primitive mantle except Rb and Pb which are in excess by 28\% and 21\%, respectively. This scenario is no doubt overly simplistic. For one, there is no real evidence for the existence of a primitive mantle reservoir (see review by Van Keken et al. [73]). However, there is evidence for a lower mantle that is less depleted than DMM, but depleted nonetheless; this reservoir is implied from many OIB isotopic arrays and termed FOZO by Hart et al. [74]. If a depleted lower mantle were accounted for here, the DMM reservoir would be significantly smaller than 33\% in order to allow for the moderate depletion of the lower mantle.

Scenario 2 is the mass-balance of DMM, continental crust, and recycled oceanic crust. The idea of a recycled MORB component in the mantle is corroborated by the observation that the major element composition of DMM cannot be balanced by continental crust alone (see Table 3). At 43±6\% DMM and 2.0±0.6\% parental N-MORB of Su and Langmuir [28], this scenario provides a better fit for most elements than does the first scenario; all elements here are fit to within 8\% except Rb and Pb with 20\% and 15\% excesses and Nb with a 17\% deficit. The abundance of MORB cannot be increased.
greatly without having elevated M- to HREE that cannot be compensated by adding more DMM. However, we have not considered subduction zone alteration of oceanic crust, which almost certainly affects this mass balance.

Scenario 3 is the mass-balance of DMM, continental crust, recycled oceanic crust, and an OIB source component (from Workman et al. [75]). To show upper limits on the sizes of enriched mantle components, the mass balance calculation has been made assuming 0% primitive mantle. The resulting balance is 74±5% DMM, 4.7±1.0% MORB, and 21±5% OIB source; all elements are fit to within 15% except Rb and Nb with 23% excess and 21% deficit, respectively.

In each scenario 2 and 3, the fraction of MORB in the mass-balance is less than the mass of oceanic crust generated throughout Earth history (6–7% of the mantle mass, assuming constant rates for 4.55 Ga). As such, it is suggestive of the mantle being partially cannibalistic with respect to subducted oceanic crust. However, these mass balances do not include a depleted lithosphere, and could therefore be misrepresentative if oceanic crust and lithosphere are shown to be absolutely mechanically and thermally coupled.

5. Conclusions

Through abyssal peridotite trends, the isotopic composition of N-MORB and a few canonical ratios, we have constructed a major and trace element reference model for average, unmelted, depleted MORB mantle (DMM). From this DMM, parental MORB is generated by about 6% aggregated fractional melting as constrained primarily from the enrichment factor for the highly incompatible elements in parental MORB. Melting occurs mainly in the spinel facies mantle, but is most likely initiated within the uppermost garnet facies, as suggested by pHMelts model runs. The water content inferred by the derived trace element composition is between 70 and 160 ppm, and is an integral ingredient in modeling mantle melting [70] and mantle viscosity [67,68]. We have provided trace element compositions for minerals in the uppermost mantle which can be better estimated in the future with increasingly accurate information on mineral/mineral partitioning of trace elements and compositional variations of minerals with temperature and pressure.

The radiogenic heat production of DMM (from U, Th, and K) is only 15% that of the bulk silicate Earth at 2.43×10⁻⁹ W/m³, using a density of 3.20 g/cm³ and radiogenic heat production values from Durrance [76]. It takes ~33% of the mantle mass to be composed of DMM, the remaining being primitive mantle, to balance the continental crust alone, and ~43% if including an oceanic crust component. If there is no primitive mantle, the maximum masses of the oceanic crust and OIB reservoirs are 5% and 21%, respectively, if these enriched reservoirs are balanced purely by DMM.

Overall, the composition constructed here is a robust estimate for average upper mantle and can be used as an input parameter for a variety of models concerning mantle processes.

Acknowledgements

We are endlessly grateful to Henry Dick, whose decades of toils over mid-ocean ridges and abyssal peridotites have made possible the work presented here; in jest we question his sanity for counting over half a million points on abyssal peridotite modal abundances. Many stimulating conversations have been had with Nobu Shimizu, Jessica Warren, Glenn Gaetani, Peter Kelemen, and Greg Hirth on the nature of the depleted mantle. We especially thank Paul Asimow for a sneak-preview application of his new pHMelts model, as well as E. Hauri and W. McDonough for their helpful reviews.

Appendix A. Supplementary data


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