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Dynamical geochemistry of the mantle

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Abstract

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Despite progress in reconciling refractory trace elements and isotopes with the structure and dynamics of the mantle inferred from geophysical constraints and dynamical modelling, mass balances of key elements and observations of noble gases in the mantle have remained enigmatic. This paper reviews arguments that most issues can be resolved if the full implications of the major-element heterogeneity of the mantle are taken into account.

A reconciliation of refractory trace elements and their isotopes with the dynamical mantle, proposed and quantified by Hofmann, White and Christensen, has been strengthened by work over the past decade. The apparent age of lead isotopes and the broad refractory-element differences among and between ocean island basalts (OIBs) and mid-ocean ridge basalts (MORBs) can now be quantitatively accounted for with some assurance.

It has been proposed recently that noble gases reside in a so-called hybrid pyrox-¹⁵ enite assemblage that is the result of melt from fusible pods reacting with surrounding refractory peridotite and refreezing. Hybrid pyroxenite that is off-axis may not remelt and erupt at MORs, so its volatile constituents would recirculate within the mantle. Hybrid pyroxenite is likely to be denser than average mantle, and thus some would tend to settle in the D" zone at the base of the mantle, along with some old subducted oceanic ²⁰ crust. Residence times in D" are longer, so the hybrid pyroxenite there would be less

degassed. Plumes would sample both the degassed, enriched old oceanic crust and the gassy, less enriched hybrid pyroxenite and deliver them to OIBs. This model can account quantitatively for the main He, Ne and Ar isotopic observations, and for the poor correlation of unradiogenic gases with refractory-element enrichment in OIBs.

The difficulty with mass balances can be traced to the common inference that the MORB source is strongly depleted of incompatible elements, which leaves a deficit of key elements and seems to require a hidden reservoir that is enriched and undegassed. However it has recently been argued that conventional estimates of the MORB



source composition fail to take full account of mantle heterogeneity, and in particular focus on an ill-defined "depleted" mantle component while neglecting less common enriched components. Recent estimates have also been tied to the composition of peridotites, but these probably do not reflect the full complement of incompatible elements in the heterogeneous mantle. New estimates that account for enriched mantle components are capable of satisfying mass balance requirements, although some additional uncertainties apply to argon. The result is that the MORB source is depleted by only about a factor of 2, relative to the primitive Earth.

1 Introduction

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- ¹⁰ As the physical structure and dynamical behaviour of the mantle have become clearer, several aspects of mantle geochemistry have remained enigmatic, leading to divergent models that have not simultaneously satisfied the geophysical and geochemical constraints. Whereas geophysical inferences have led to a picture of the mantle with no major vertical compositional variation, apart from the D" zone in the lowest 200– ¹⁵ 300 km (Davies and Richards, 1992; Davies, 1999b; Grand et al., 1997), geochemical
- constraints have frequently been deemed to require a thick, hidden layer relatively enriched in incompatible elements, including the noble gases, in order to satisfy mass balance requirements (Allegre et al., 1996; Kellogg et al., 1999). Such a layer is not only not required by the geophysical evidence, it is precluded, though this has not been widely appreciated. An alternative resolution of the mass balance question is reviewed
- later in this paper.

The refractory trace elements and their isotopes have by now been quite well reconciled with the geophysical mantle, apart from the mass balance question, starting from the hypothesis of Hofmann and White (1982). They proposed that ancient, sub-²⁵ ducted oceanic crust is recycled to the Earth's surface via the D" zone and mantle plumes, and they argued that the enrichment of many OIBs relative to MORBs was due to this component of old oceanic crust. This scenario was quantified by



Christensen and Hofmann (1994) using numerical models, and they found that subducted oceanic crust, which is denser than average mantle, does indeed tend to segregate to the bottom, and that its average residence time was permissive of the apparent age of 1.8 Ga evident in lead isotopes. Subsequent work, reviewed here, has recti-

⁵ fied some deficiencies in Christensen and Hofmann's pioneering modelling, has found that appropriate residence times occur quite generally and has thus strengthened the quantitative case supporting this interpretation.

The place of noble gases in the mantle has been one of the most enigmatic aspects of mantle geochemistry, and no really satisfactory resolution has been proposed in either geochemical or geophysical scenarios. Recently it has been argued (Davies, 2010) that the resolution can be found starting from the widely-accepted expectation that the mantle is heterogeneous on many scales in both major and trace elements. This strongly affects mantle melting, melt migration and the extraction of incompatible elements from the mantle.

A resolution of the mass balance question may also be found by following the implications of mantle heterogeneity (Davies, 2009b). This will be reviewed later.

One major question about the mantle's composition remains. The abundance of heat-producing elements (principally U, Th and K) does not seem to be sufficient to sustain the thermal evolution of the mantle obtained from conventional thermal evo-

²⁰ lution calculations, either parameterised or numerical. Several possible resolutions of this question have been advocated, and they will be briefly discussed. However the question seems yet to be persuasively resolved.

2 The geophysical mantle

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The broad structure of the mantle inferred from geophysical constraints is illustrated in Fig. 1, with dynamical elements and schematic geochemical heterogeneity (Davies, 1990a). Included are subducting lithosphere and rising mantle plumes, each of which is the active component of a mode of mantle convection (Davies, 2011, 1999b).



The only significant vertical compositional variation is at the base, where the socalled D" layer, about 200–300 km thick, is interpreted to be compositionally denser and also probably to have a phase transformation within it (Lay et al., 1998; Hirose, 2006). It is also, by inference, part of a thermal boundary layer where heat is conducting from the core (Lay et al., 2008). A suggestion in the sketch of a gradient of heterogeneity through the lower third of the mantle is not sustained in the discussion to follow.

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The possibility of a compositional change through the transition zone, and especially at the 660-km seismic discontinuity, was resolved in the negative by two arguments.

- The first (Davies, 1988a) is that such a compositional boundary would also be a boundary separating two convection layers. Heat would therefore have to conduct through the boundary, generating a hot thermal boundary layer above the 660-km boundary. Because little heat is inferred to be generated within the upper mantle, much of the Earth's heat budget would have to come from deeper, and would therefore be passing
- through this boundary layer. It would therefore generate buoyant upwellings whose strong buoyancy would generate surface topography comparable to the topography of the mid-ocean ridge system. No such topography exists. The only topography attributable to buoyant upwellings is the hotspot swells, whose amplitude implies quite directly that the upwellings generating them carry less than about 10% of the Earth's heat budget. This is consistent with current estimates of the heat coming from the core
- 20 heat budget. This is consistent with current estimates of the heat coming from the core (Lay et al., 2008; Leng and Zhong, 2008), and implies that mantle plumes rise without major impediment through the whole mantle.

The second argument is that seismic tomography detects subducted lithosphere extending from surface subduction zones through the transition zone and deep into the lower mantle (Grand et al., 1997). Although it was the striking images from this study that persuaded many people that mantle convection operates as a single layer, both arguments are strong, and the first argument applies also to other proposed layers in the mantle, as we will see later. From the first argument also comes an important constraint on the composition of the MORB source.



This mantle structure is capable of explaining the main dynamical features of the mantle, plate tectonics and mantle plumes, which are both forms of mantle convection. The form and kinematics of tectonic plates is explained by their effectively brittle rheology (Davies, 1988b; Wilson, 1965). The motion of plates is explained by the negative buoyancy of subducting plates (Turcotte and Oxburgh, 1967; Davies and Richards, 1992). Mantle plumes are a straightforward consequence of heat conducting from the core, and they explain the main features of volcanic hotspots and flood basalt eruptions (Davies, 1988a; Leitch and Davies, 2001; Campbell and Griffiths, 1990; Griffiths and Campbell, 1990). These points are also covered in Davies (2011, 1999b).

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The question reviewed in this paper is whether geochemical observations of the mantle can be reconciled with this broad picture of mantle structure and dynamics.

3 Refractory trace elements

The roles of refractory trace elements and their isotopes in the mantle model just outlined are by now relatively well understood, following the hypothesis of Hofmann and
¹⁵ White (1982) and the pioneering modelling by Christensen and Hofmann (1994). Further theoretical and numerical modelling over the past decade has strengthened the case for the Hofmann and White hypothesis, in which some subducted oceanic crust settles to the base of the mantle, later to be entrained in mantle plumes and contribute to eruptions at volcanic hotspots. Simple calculations, validated by numerical models,
²⁰ estimate the fraction of the mantle that has been processed through the melting zones under mid-ocean ridges and the proportion of subducted oceanic crust to be expected in the mantle. Extensions of such calculations, complemented by numerical models of various kinds, elucidate the factors that control the age distribution of subducted oceanic crust and its mean age in different mantle contexts.



3.1 Fraction of mantle processed

Mid-ocean ridges are the sites of mantle melting and the segregation of melt to form the oceanic crust, leaving a depleted zone below. The depth of main melting (i.e. the depth to the dry solidus) is about 60 km, but minor melting or melting of heterogeneities might

⁵ occur as deep as 110 km (Yasuda et al., 1994; Spandler et al., 2008). The present areal rate of seafloor spreading is 3 km² yr⁻¹ (Parsons, 1982). The rate at which mantle mass is being processed through the MOR melting zone can then be calculated as

 $\varphi = \rho A_{\rm S} d_{\rm m}$

where ρ is the density of the upper mantle, A_S is the areal spreading rate and d_m is the melting depth. The time it would take to process one mantle mass, M, at this rate is then

 $\tau = M/\varphi$

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This can be called the mantle processing time (Davies, 2002). With the above spreading rate, $d_{\rm m} = 110$ km, a density of 3300 kg m⁻³ and a mantle mass of 4 × 10²⁴ kg, the processing time is about $\tau = 4$ Gyr.

Because of higher radioactive heating in the past, the mantle would have been hotter, would have had a lower viscosity and so would have overturned faster. Davies (2002) estimated that, at present rates of overturn, it would have taken about 18 Gyr to accomplish the number of overturns that have actually occurred within 4.5 Gyr. A "model time", t_m , was defined to run in proportion to the rate of overturn. Davies also showed that the proportion, p, of the mantle that remains unprocessed declines exponentially with t_m :

 $\rho = \exp\left(-t_{\rm m}/\tau\right)$

After $t_{\rm m} = 18$ Gyr, with $\tau = 4$ Gyr, $\rho = 0.011$.

Thus by this estimate only about 1% of the mantle remains primitive. This fraction would be even smaller if the melting depth was greater in the past, because the mantle



(1)

(2)

(3)

was hotter. Numerical calculations yielded results consistent with this result (Davies, 2002). Thus most of the mantle will have been processed through the melting zone, and we cannot expect a significant amount of primitive, unmelted mantle to have survived in the MORB source.

5 3.2 Expected mantle heterogeneity

It is widely acknowledged that the mantle is heterogeneous in major element composition and in mineral assemblage or lithology. In the upper mantle it is predominantly peridotite, with smaller proportions of eclogite and pyroxenite (Ringwood, 1975; Hofmann, 1997). With the advent of plate tectonics a straightforward explanation for this became evident: a subducting plate is a layered structure, with mafic oceanic crust on top and an ultramafic (peridotite) mantle section underneath, the latter variably depleted of the components removed by melting to form the crust. At depth the oceanic crust will exist as eclogite, and mantle convection will stir the two kinds of material.

One can readily estimate the amount of oceanic crust that has been subducted over time, but it will also have been removed by melting at mid-ocean ridges. As the amount builds up from zero in the mantle due to subduction, so more will melt, until an equilibrium is approached. Using logic similar to the previous section, the proportion of subducted crust in the mantle, *f*, will exponentially approach a maximum $f_{\rm m} = \varphi_{\rm S}/\varphi$, where $\varphi_{\rm S}$ is the rate of subduction of oceanic crust:

²⁰ $\varphi_{\rm S} = \rho_{\rm c} A_{\rm S} d_{\rm c}$

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where ρ_c is the density of oceanic crust and d_c is its thickness. Then at any model time, the proportion of crust in the mantle will be

 $f = f_{\rm m} \left[1 - \exp\left(-t_{\rm m}/\tau\right) \right]$

After 18 Gyr of model time *f* will be 99% of f_m , and with a crustal density of 2900 kg m⁻³ and thickness of 7 km this gives f = 0.06. In other words the mantle should contain about 6% of subducted, unprocessed oceanic crust. As we will see later, not all crust Discussion Paper SED 3, 249-333, 2011 Dynamical geochemistry of the mantle **Discussion** Paper G. F. Davies **Title Page** Introduction Abstract Conclusions References Discussion Paper Tables Figures Back Close **Discussion** Paper Full Screen / Esc Printer-friendly Version Interactive Discussion

(4)

(5)

melted under ridges may have been removed from the mantle, so the total amount of crust-derived material may be about double this.

This result quantifies the expectation that, after several billion years of subducting oceanic crust plus underlying depleted mantle, the mantle will have substantial majorelement heterogeneity. Because the oceanic crust is enriched in incompatible trace elements relative to the mantle, this implies heterogeneity of trace elements as well.

3.3 Stirring versus homogenising

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After the lithosphere has subducted, it will be stirred around the mantle by mantle convection. It has been a common presumption that the material will then be homogenised

- ¹⁰ by mantle stirring. This presumption was behind early interpretations of trace-element heterogeneity: heterogeneity was taken to imply the existence of separate reservoirs in the mantle, because a convecting layer ought to be compositionally homogenised (Wasserburg and DePaolo, 1979). There are two reasons why this presumption is quite misleading.
- ¹⁵ First, rates of stirring in the mantle are very slow. (By "stirring" I mean here the intermingling of two kinds of material.) This is not only because mantle convection is slow, it is also because it involves only "cells" of the largest scale. In familiar fluids, such as water, momentum is significant compared with viscosity, and the result is that when water is stirred a cascade of vortices forms, down to quite small sizes. That is
- ²⁰ why a mixture of coffee and cream can be quickly homogenised. However in fluids in which viscosity is dominant, such small-scale vortices do not form, and the stirring must be accomplished only by the largest scale of flow. Imagine stirring a mixture of cream and cold honey: the fluids will intermingle, but will require much more stirring to be homogenised.

²⁵ The second reason homogenisation is very slow in the mantle was pointed out quite a long time ago: solid state diffusion rates are very slow, such that it will extend only over centimeters within a billion years (Hofmann and Hart, 1978). Unless the solid



materials can be stretched and thinned down to the scale of centimeters, they will remain compositionally distinct for the age of the Earth.

3.4 Processing time versus homogenising time

Lead isotopes from the mantle form an array (Fig. 2) whose slope can be interpreted as corresponding to an age of about 1.8 Ga (Hofmann, 1997; Chase, 1981). This implies in turn that mantle heterogeneities persist for this order of time. The apparent lead age has been interpreted in two different ways. One interpretation was that it represents the average time it takes to homogenise heterogeneities in the mantle. The other is that it is the average time between passages through a MOR melting zone, which would be the processing time defined in Eq. (2).

The homogenising time is quite sensitive to details of the flow, even if the flow is highly viscous. If mantle convection is unsteady and confined to the upper mantle, the homogenising time might be as short as 400 Myr (Kellogg and Turcotte, 1990), whereas if mantle convection is relatively steady and occupying the whole mantle then

- ¹⁵ heterogeneities persist for billions of years (Gurnis and Davies, 1986). Stirring is faster in three-dimensional flow than in two-dimensions (van Keken and Zhong, 1999). As a result it has been difficult to show how the heterogeneity might survive for the required time, i.e. how the homogenising time might correspond with the observed apparent lead age.
- ²⁰ On the other hand, in the numerical modelling of Christensen and Hofmann (1994), and later work summarised below, the presumption has been that the apparent lead age represents the processing time. It is by now plausibly established that this interpretation is consistent with relevant observations, as we will see.

3.5 Trace element heterogeneity in MORBs and OIBs

²⁵ OIBs typically have much higher concentrations of refractory incompatible trace elements than MORBs, though those from Hawaii are intermediate. Such observations



are summarised in Fig. 3. It was this difference that motivated Hofmann and White (1982) to argue that OIBs contain a component of old oceanic crust that has been cycled through the mantle by subduction and subsequently returned in a mantle plume, spending some of the intervening time within the D'' layer.

- ⁵ Christensen and Hofmann (1994) tested this hypothesis with a numerical model in which subducted oceanic crust was simulated with tracers carrying extra mass, to account for the higher density of subducted crust through most of the depth of the mantle (Hirose et al., 2005). They found that some of the subducted crust did indeed accumulate at the base of the model, though much of it remained suspended in the mantle
 ¹⁰ interior. An example illustrating this behaviour from a more recent calculation (Davies, 2008) is chosen in Fig. 4. Such models clearly support the Mefmone and White hypotheses.
- 2008) is shown in Fig. 4. Such models clearly support the Hofmann and White hypothesis, as they provide an accumulation of old oceanic crust in the D" region, where it might be entrained by plumes and ultimately contribute to OIBs.

However it is difficult to further quantify the process, for example by calculating how ¹⁵ much old crust might be entrained into a plume, and how the elements might be partitioned as the plume melts near the surface. There will be a limit to how much negatively buoyant crust material can be lifted by the thermal buoyancy of a plume, and the two kinds of buoyancy can induce complicated behaviour in a thermochemical plume, with the heavier material tending to drop out in the upper mantle (Farnetani and Samuel, 2005; Lin and you Koken, 2006; Kumagai et al., 2008). Detailed medals of melting

20 2005; Lin and van Keken, 2006; Kumagai et al., 2008). Detailed models of melting near the surface will be difficult because the plume will be intrinsically heterogeneous (Kerr and Mériaux, 2004), a topic that will be discussed later.

3.6 Isotopic heterogeneity

The observed heterogeneity of lead isotopes is shown in Fig. 2, and the observed heterogeneity of neodymium and strontium isotopes is shown in Fig. 5, with symbols defined as in Fig. 2. These plots show that both OIBs and MORBs have a range of isotopic composition, though the MORB range is smaller by about a factor of two. Most



of the variations evident in OIBs are also evident in MORBs, though with a smaller spread.

Isotopic heterogeneity occurs on all spatial scales, from global to grain-size. Heterogeneity of MORBs at the largest scale is evident in Figs. 2 and 5, where differences

- ⁵ can be seen particularly between the Indian Ocean and the Pacific Ocean, with the Atlantic Ocean tending to be intermediate. Heterogeneity at intermediate scales, down to a few degrees of latitude, are evident along the Mid-Atlantic Ridge, Fig. 6. There are variations at the scale of a few degrees comparable to the variation along the entire ridge, for example near 14° N. Large variations have also been found within single
 ¹⁰ hand specimens (Hofmann, 2003), suggesting that such variations are present in the source, though they will tend to be homegonized within magma chambers during examples.
- source, though they will tend to be homogenised within magma chambers during extraction.

 Christensen and Hofmann (1994) and some later modellers (Xie and Tackley, 2004; Brandenburg et al., 2008) have calculated synthetic isotope plots from numerical mod els for comparison with observations. While this is a laudable approach in principle, Davies (2002) noted that there are considerable uncertainties in melting relationships, melt migration processes and scales of sampling that weaken these plots as probes of the source heterogeneity.

3.7 Sampling heterogeneity versus mixing reservoirs

- ²⁰ The interpretation of plots of isotopic heterogeneity was influenced early by the common assumption that convecting layers would be homogenised. As a result the MORB data were frequently characterised as "remarkably uniform", but this owed more to circular definitions than to the actual spread of data, a point also emphasised by Hofmann (2003). The conception of homogenised convecting layers also implied to many
- that separate mantle reservoirs would be required to maintain heterogeneity. Consequently the spread of data in Figs. 2 and 5 was widely assumed to be due to mixing between end members, and much debate focussed on how many end members were necessary.



However homogenising times can be very long in mantle convection, as noted above, so heterogeneity in itself does not require separate reservoirs. The absence of geophysical evidence for mantle reservoirs, apart from D'', and the continuous generation of mantle heterogeneity by subduction suggest an alternative interpretation of isotopic heterogeneity. Rather than representing mixing, the spread of data may directly reflect the spread of values in the source region.

This shift of perception has a large effect on how the mantle is interpreted. It is illustrated in Fig. 7. In the mixing interpretation, Fig. 7a, the emphasis is on identifying the extreme values, the "end members". In the direct sampling interpretation, the important parameters are the mean value and the spread. The notion of end members is not relevant. If end members are disposed of, then the huge emphasis on characterising a putative "depleted MORB mantle" is also disposed of. Instead, the more meaningful measure is the mean value, and it is the mean value that governs mass balances and the amount of heat generated in the mantle, topics that will be discussed in Sect. 6. Similarly, the focus on a putative "undegassed" end member of noble gas distributions

Similarly, the focus on a putative "undegassed" end member of noble gas distributions is replaced by a focus on mean and spread.

3.8 Residence times

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Christensen and Hofmann (1994) obtained mean residence times of 1.3–1.6 Gyr from their numerical models of subduction, stirring and settling of oceanic crust. On the other

²⁰ hand Davies (2002) obtained mean residence times of 2.2–2.7 Gyr for MORBs and 2.6–3.4 Gyr for samples from the bottom accumulations of heavy tracers. Huang and Davies (2007a, b) later obtained intermediate ages from three-dimensional models.

On the one hand these results seem to demonstrate that mantle heterogeneities can plausibly survive for the order of the two billion years indicated by lead isotopes.

²⁵ However the discrepancies among the results were concerning. Two factors have been found to explain the discrepancies.

First, the model must be run for an appropriate time. Christensen and Hofmann's models were run for only 3.6 Gyr, and with steady convection rates. Because the



mantle was likely to be hotter in the past, convection and plates would have been faster and the mantle would have been processed more rapidly. As described in Sect. 3.1, models running at present rates would need to be run for about 18 Gyr to achieve a comparable amount of processing. Christensen and Hofmann's models fall well short

- ⁵ of this. The average residence time exponentially approaches a steady value with "model time" (analogous to the logic of Sects. 3.1 and 3.2). When converted to real "Earth time", the residence time continues to increase because of slowing convection, and its rise is shown in Fig. 8a. Even after 4.5 Gyr of Earth time, the residence time is still increasing at a significant rate.
- Second, the processing time scale of the model should match the processing time scale of the mantle. It turns out that the earlier numerical models had a range of processing time scales because of different assumptions about melting depth and because they ran with various plate speeds. The processing time of Davies (2002) was 7.2 Gyr, whereas it was only 1.5 Gyr in Christensen and Hofmann (1994). The relationship between the processing time and the final residence time (after 4.5 Gyr of Earth time).
- tween the processing time and the final residence time (after 4.5 Gyr of Earth time) can be calculated from a sampling theory outlined below, and it is shown in Fig. 8b. This shows that all the model results are reasonably consistent once the different processing times are accounted for. The processing time of the mantle was estimated (Sect. 3.1) to be about 4 Gyr, and this would predict a mean residence time of MORBs
 of about 1.8 Gyr.

Figure 8b synthesises results from a wide range of numerical models: two dimensional and three dimensional, in rectangular or spherical geometry (including full spherical and regional spherical), at low, moderate or high Rayleigh numbers, with various viscosity structures, and steady or evolving from an early hot state. For example a higher viscosity in the lower mantle does not significantly extend residence times. An example of a 3-D spherical model with "heavy" tracers is shown in Fig. 9. Figure 8b

shows that the main determinant of residence time is the processing time scale, τ , defined in Sect. 3.1. Whereas the other factors can have large effects on the homogenising time scale, they have only secondary effects on the residence time. This



is an important insight that makes the interpretation of mantle geochemistry more accessible.

3.9 Sampling theory

In Sects. 3.1 and 3.2, Eqs. (3) and (5) are derived by assuming that a kind of mantle material will be sampled by a MOR melting zone in proportion to the amount of that material already in the mantle. Thus for example the proportion of primitive mantle declines with time, so the rate at which primitive material melts also declines, yielding the exponential function of Eq. (3). This theoretical result is useful for interpreting numerical models, for example by confirming the numerical result that very little primitive material survived to the present (Davies, 2002). This approach has been extended in a number of ways by Huang to further elucidate the behaviour of the models, and the mantle (Huang and Davies, 2007a, b, c).

Davies (2002) found that the MORB sample of tracers had a wide range of ages from a few hundred million years to 4.5 Ga, even though the mean age was about 2.7 Ga. This result is important for interpreting noble gases, which will be discussed later. An

example of a histogram of MORB ages is shown in Fig. 10.

The fraction, f_i , of tracers with ages between a_i and $a_i + \Delta a_i$ can be derived from the sampling theory as

$$f_i = \frac{\Delta a_i}{\tau} \exp\left(-\frac{a_i}{\tau}\right)$$

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The distribution calculated from this formula is shown in Fig. 10 (solid grey line). It 20 has the same general form as the numerical distribution, except the latter has a gap at younger ages and the rest of the histogram is slightly larger than the theoretical curve.

The absence of young tracers in the numerical distribution is plausibly due to the fact that tracers must traverse the distance from a subduction zone to a spreading center before they can be sampled. Thus the sampling is not as random as assumed implicitly in the initial sampling theory. This can be taken into account in the sampling theory by



(6)

excluding the younger part of the distribution and calculating proportions of the rest in each age range. The result (Huang and Davies, 2007a) is shown in Fig. 10 as the dashed grey line, with the sampling delay adjusted to match the numerical gap. The result is an excellent fit to the numerical distribution with a theory that requires only two input parameters: the processing time, τ , and the sampling delay time.

From the age distribution, the mean age can be calculated. The result, with zero delay time, is

 $a_{\rm tr} = \tau \left[1 - \exp\left(-t_{\rm m}/\tau\right) \right]$

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where t_m is model time. The conversion to Earth time must be done for each age range before a mean is calculated. The expression with sampling delay is more complicated (Huang and Davies, 2007a). The variation of this mean age with Earth time is included in Fig. 8a (heavy dashed curve), where it follows the numerical result fairly closely. Taking account of a processing delay would reduce the discrepancy (not shown). The variation of mean age with processing time is included in Fig. 8b (solid curve). Fig-

¹⁵ ure 8b also includes two curves that include the effect of a sampling delay of 0.4 Gyr (dashed) and 1.2 Gyr (dash-dot). The set of theoretical curves in Fig. 8b reasonably span the results from a range of numerical models, and so confirm that the main control on the mean age is the processing time.

In models in which the tracers are "heavy", i.e. which include a small mass anomaly equivalent to the excess density of subducted oceanic crust relative to mean mantle, the mean ages of the OIB samples are larger than the MORB ages. This is presumably due to some of the heavy material being trapped, at least temporarily, in the accumulation at the bottom. The sampling theory has been extended to account for this by assuming a population of tracers that are permanently trapped (Huang and Davies,

²⁵ 2007b). The "OIB" sample is then taken to be a mixture of trapped tracers and freely circulating tracers. This theory involves a few more assumptions, but a plausible account can be derived. The dashed "OIB" curves in Fig. 8a are calculated from this theory for cases in which the subducted oceanic crust is 50 and 100 Mg m⁻³ denser than average mantle, and they give a good account of the numerical results.



(7)

3.10 Evolving processing rates

Computer power limited some 2-D (Christensen and Hofmann, 1994) and 3-D (Huang and Davies, 2007a, b) models to low, steady Rayleigh numbers. More recently, evolving 2-D models have been run at full resolution for the age of the Earth (Xie and Tack-

⁵ ley, 2004; Davies, 2008), including the slow cooling of the mantle and the resulting decrease in the depth of melting under MORs. Some studies have included the latter effect, even though the models were limited to steady Rayleigh number, in 2-D (Davies, 2002) and 3-D (Huang and Davies, 2007c). The decreasing depth of melting means the processing rate decreases and the processing time scale, τ , increases with time. The latter study is in spherical geometry at the present mantle Rayleigh number, with significant temperature-dependence of viscosity and with more realistic plates simulated (Fig. 11), so it addresses the robustness of previous findings of stirring and processing in a more realistic manner than other studies.

Huang extended the sampling theory to take account of the evolving processing time scale, which changes from 1.98 Gyr at the beginning to 4.32 Gyr at the end. Figure 12 shows the degree of processing and the MORB and OIB ages from this model, and from variations on the theory. The theory with variable τ fits the numerical results quite well throughout the evolution of the model. For comparison, predictions of the theory with constant τ are included, using the initial and final values.

The cumulative percentage of processed tracers is better described by the initial processing time scale, which makes sense because most of them are processed early anyway. On the other hand the final MORB and OIB ages are a little better described by the final processing time scale. In other words, the MORB and OIB ages are controlled more by the recent processing rate than by the early processing rate.

25 3.11 Conclusions, refractory elements

The numerical models of mantle stirring are complex enough that the reasons for their behaviour are not always obvious. The value of the simplified sampling theory is that



it allows the behaviour of numerical models to be understood with some confidence. The resulting insights can then be transferred to the mantle with greater confidence. For example, the concordance between numerical results and a fairly simple theory in Fig. 8b strengthens confidence in the conclusion that the main control on residence time is the processing time or, equivalently, the rate of processing through MOR melting zones.

The concordance between the resulting preferred numerical processing time and the observed lead apparent age then strengthens confidence that the numerical models are giving a reasonable representation of the mantle. Two of the primary characteristics of refractory elements and their isotopes can thus be reasonably accounted for by the kind of dynamical model inferred in Sect. 2, namely the difference in trace element concentrations between MORB and OIB and the apparent age of around 1.8 Gyr. The question of mass balances of these elements will be taken up in Sect. 6 after melting

¹⁵ 4 Melting in a heterogeneous mantle

of a heterogeneous mantle is considered in more detail.

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The discussions in Sect. 3 of the expectation of mantle heterogeneity, from the subduction of heterogenous lithosphere, and the observations of heterogeneity (Figs. 2, 5, 6) establish heterogeneity as a primary feature of the mantle. The heterogeneity occurs at all length scales, and it involves major elements as well as minor and trace elements and isotopes. The major-element heterogeneity is expressed as a heterogeneity of lithologies, more specifically as pyroxenite and eclogite streaks and pods in a matrix of peridotite (Ringwood, 1975; Allegre and Turcotte, 1986).

Eclogites and pyroxenites melt at lower temperatures than peridotite (Fig. 13), so as mantle rises under a mid-ocean ridge the eclogite and pyroxenite inclusions will melt

first. Melt from such inclusions will be out of chemical equilibrium with the surrounding peridotite, so if it escapes it will react, and possibly refreeze (Spandler et al., 2008; Yaxley, 2000). The product of such reactions may vary from lherzolite through pyroxenite,



garnet pyroxenite or even eclogite, depending on the relative proportions of melt and peridotite. For conciseness I refer to the products as *hybrid pyroxenite*.

Because of the back-reaction and possible freezing, the migration of melt from an eclogite pod through the peridotite matrix may be an erratic affair: some may immedi-

- ately refreeze, some may remelt at a shallower level, some may combine, at shallow levels, with melt from peridotite and be erupted in that form, some may form a reaction zone that insulates later melt from reaction and allows it to travel, and even to escape to the surface, and some may remain trapped in the mantle. These possibilities are illustrated in cartoon form in Fig. 14.
- ¹⁰ For material rising under the axis of a mid-ocean ridge, these complications might not matter much, because any refrozen material would be likely to remelt at a shallower level and ultimately mix with melt from peridotite. The end product could be nearly fully equilibrated, and indistinguishable from melt from a homogenised source of the same bulk composition.
- However for material rising off-axis, the full range of possibilities is likely to eventuate, in some proportion or other. Thus some eclogite or pyroxenite melt might reach the surface with a recognisable signature of its source, some may homogenise with peridotite melt, and some may remain refrozen and trapped. Kogiso et al. (2004) estimate that melt from pods that are silica saturated and thicker than a few meters is likely to be able to migrate significant distances through the mentle. Evidence in MORPA and
- ²⁰ be able to migrate significant distances through the mantle. Evidence in MORBs and flood basalts for a contribution from eclogite or pyroxenite sources has been adduced for example by Takahashi et al. (1998) and Sobolev et al. (2007, 2005). Melt from smaller bodies and silica-undersaturated bodies is more likely to be trapped.

The greater depth of melting of eclogite and pyroxenite enhances the likelihood of ²⁵ melt trapping. This is clarified by comparing pictures of homogeneous and heterogeneous melting under a mid-ocean ridge. The older view of melting of a homogeneous source is illustrated in Fig. 15a. Melting begins when upwelling solid mantle reaches a depth of about 60 km ("Peridotite melt zone"), and it stops (or reduces to minor rates) as the mantle flow turns horizontal and the material stops decompressing. Melt generated



in the melt zone is strongly focussed to the mid-ocean ridge by the low pressure induced by the diverging mantle flow (Spiegelman and Reynolds, 1999), thus defining a "Melt extraction zone".

If the mantle is heterogeneous, this picture is modified in several ways (Fig. 15b).
⁵ Eclogites and hybrid pyroxenites begin to melt much deeper than peridotite, about 110 km (Fig. 13), so their melting zone will be much wider. Heterogeneities further from the spreading axis may not rise shallow enough to remelt, nor may they rise into the peridotite melting zone. This material may be carried away laterally without remelting (Fig. 15b). The eclogite melting that occurs outside the peridotite melting zone will tend to be in disconnected pockets. Melt from larger eclogite bodies may migrate, but much of it still may not reach the surface.

Eclogite that rises under the peridotite melt extraction zone is more likely to be extracted because the peridotite melting will tend to form a connected zone of melt within which porous flow may occur. Any eclogite melt that enters this zone is likely also

to move by porous flow and to mix with the peridotite melt. The melt extraction zone may be narrower than in the homogeneous case, if the total melt productivity of the heterogeneous source is greater: the observed volume of melt, to form the 7-km-thick oceanic crust, would by implication be drawn from a deeper, narrower zone. This would enhance the likelihood of off-axis melts being trapped. Even some off-axis peridotite melt could be trapped in this way.

The tendency of off-axis melt to be trapped will also be enhanced if the peridotite matrix is more refractory than the "fertile peridotite" usually assumed in models of the melting of a homogeneous source. This is because the refractory peridotite melting would begin shallower than 60 km and so be even less likely to capture the pyroxenite products.

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Thus significant amounts of hybrid pyroxenite are likely to be trapped, and then recirculated within the mantle. Over time some of it will return to MORB melting zones, potentially to be remelted. Thus there will be multiple generations of hybrid pyroxenite, and a significant population of it may accumulate, as foreshadowed in Sect. 3.2. The



material entering melting zones will then have three main components, not two: peridotite residue, subducted oceanic crust and hybrid pyroxenite. Incompatible elements will be carried by both the subducted oceanic crust and the hybrid pyroxenite. The two types of heterogeneous inclusion are depicted schematically in Fig. 15b.

- ⁵ Two fundamental implications follow from this picture. One is, as already stated, incompatible elements will over time become concentrated in the heterogeneous inclusions, i.e. the subducted oceanic crust and the hybrid pyroxenite. The other is that the bulk extraction of incompatible elements will not be governed only, or even mainly, by local chemical partition coefficients. These points will be briefly elaborated.
- ¹⁰ The Earth is expected to have formed hot, due to the release of gravitational energy of accretion, and especially the hypothesised moon-forming giant impact, which may have melted most or all of the Earth (Melosh, 1990). A magma ocean would have cooled within only tens of thousands of years, though large impacts would reform magma lakes frequently (Davies, 1990b). Although a lot of melting would have
- taken place, the liquid and solid mantle regimes would have been highly dynamic, and competing mixing processes would have tended to prevent major differentiation and stratification of the mantle (Stevenson, 1990). The difficulty of finding any surviving remnant of such differentiation provides some evidence for this claim. The result of this early history is thus likely to have been a mantle that had undergone melting and that
- had been vigorously stirred but not completely homogenised. The melt products from the early mantle would have been broadly mafic (basaltic through komatiitic). In other words, a heterogeneous mantle, more or less like the present, may date from very early in Earth history. Consequently we could expect the mantle's incompatible elements to have been concentrated into mafic mantle heterogeneities from quite early in Earth his-
- ²⁵ tory. The peridotitic matrix surrounding the heterogeneities would be correspondingly depleted and refractory.

The residue from melting under mid-ocean ridges has commonly been inferred to be strongly depleted of incompatible elements, on the assumption that incompatible elements are efficiently stripped from solid phases and carried away by the melt. This



may be true locally within the melting zone, but if the melt does not efficiently migrate to the surface (Fig. 14) then the incompatible elements will not be efficiently removed from the melt zone. This is the picture already argued above (Fig. 15). The implication is that significant quantities of incompatible elements may remain in the residue zone.

- A simple illustration makes the point that the retention of incompatibles is probably not governed by chemical equilibrium partitioning. If an element has a partition coefficient of 0.01, then only about 1% of it will remain in the solid phase, and 99% will partition into the melt. However if only 1% of that melt fails to migrate out of the residue zone, then the amount of the incompatible element remaining in the residue zone will
- be doubled. If several percent of melt remain trapped, then the bulk abundance of the incompatible element will be several times that predicted by chemical equilibrium partitioning. The abundance will be governed instead by the vagaries of melt migration through a heterogeneous medium, in other words by a combined physical-chemical, dynamical and probably disequilibrium process rather than by pure chemical equilib-
- 15 rium.

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The incompatibilities inferred from the composition of oceanic crust will not be greatly affected by this retention, because only a few percent of the incompatible elements may be involved.

These two implications will be explored further in the rest of this review. They provide a plausible location for noble gases in the mantle, and they require a re-evaluation of the mass balances of incompatible elements and of the heating of the mantle.

5 Noble gases in the heterogeneous mantle

The place of noble gases in the mantle has been quite enigmatic. They have not fit easily into any version of mantle structure or dynamics. The essential problem and its resolution can be illustrated by helium, so it is the only one that will be considered in detail here. There is an additional question regarding the mass balance of ⁴⁰Ar, and it will be argued in Sect. 7 that the uncertainties in that mass balance are significantly larger



than have been implied in the past, and the mass balance can plausibly be accommodated within those uncertainties. The main interpretations and debates regarding the noble gases have been presented before (Allegre et al., 1987; Porcelli and Wasserburg, 1995a; Albarède, 2008; Class and Goldstein, 2005; Parman, 2007; Tolstikhin and Hofmann, 2005), and will not be canvassed at length here.

Isotopic observations of helium are summarised in Fig. 16, with observations of strontium and lead for comparison. All three data sets show that MORBs have a narrower range than OIBs. All distributions are skewed, with relatively long tails on one side.

- For Sr and Pb the OIBs tend to have more radiogenic ratios, but overlapping the MORB range. Helium, on the other hand, tends to be less radiogenic, though some values are more radiogenic. (Unfortunately the convention for He is to put the radiogenic isotope in the denominator, contrary to that for other elements.) The main difference between helium in OIBs and MORBs is the much greater range of ratios in OIBs 5–6 times bigger than for MORBs. For Sr and Pb the ranges differ by only a
- factor of 2 or so. A second difference in all three systems is that the OIB means differ from the MORB means. In the case of He, the difference is less than a factor of two.

This characterisation of helium isotopes is quite different from the conventional one. In the conventional interpretation the OIBs are taken to be tapping a "primitive, unde-

- gassed" reservoir (meaning a reservoir that has not been degassed since early in Earth history, so it has retained essentially all radiogenic products). However this assumption was an extension of the now-abandoned assumption that the lower mantle is primitive in all respects (Wasserburg and DePaolo, 1979). The mere presence of some ³He (or of more ³He in OIBs) is no reason to assume a primitive source is required, because
- ²⁵ we could not expect every last atom of ³He to have leaked out of the Earth. Without some benchmark of how much helium ought to remain in the Earth, all that can be concluded is that the source of the higher ³He/⁴He ratios has more ³He or less ⁴He, or both, than other sources.



The mass balance of ⁴⁰Ar has also been used to argue for a large "undegassed" reservoir in the mantle, comprising much or all of the lower mantle (Allegre et al., 1996). However the uncertainties in this mass balance are significant, and an alternative mass balance can plausibly be established, as will be discussed later.

- ⁵ There is in any case clear observational evidence against the primitive reservoir interpretation, which is that lead isotopes have shown all along (Davies, 1984) that the sources of high-³He/⁴He OIBs have been previously processed through a melting zone. A recent demonstration of this is shown in Fig. 17. The higher values of ³He/⁴He in fact occur in samples whose lead and neodymium isotopes are most like the more depleted
- ¹⁰ MORB samples. On the other hand the more radiogenic (low ³He/⁴He) values occur in more "enriched" samples, which may indicate the presence of recycled sediment and altered oceanic crust in the sources (Class and Goldstein, 2005; Ellam and Stuart, 2004).

Almost all previous discussions of the helium isotopes have focussed great attention on the highest value of ³He/⁴He, in contrast to the characterisation above in terms of the mean and spread of the distribution. This reflects the underlying assumption that distinct reservoirs must be involved, with the distribution reflecting mixing from two (or more) reservoirs. In that case it is the extreme values that are important (Fig. 7a). However if the observed distribution merely reflects a distribution of values in a hetero-

²⁰ geneous source (Fig. 7b), then the extreme values are of no great significance, and it is the mean and spread that are of primary interest.

So, the question is not how to fit a primitive, undegassed reservoir into the dynamic mantle. The question is how two populations of noble gases can arise that have somewhat different isotopic means and spreads. This is similar to the question raised by the

refractory-element isotopes, though the observations are different in the details already noted. Straightforward answers suggest themselves from the discussion of heterogeneous melting in the previous Section.

From the previous discussion we can distinguish two kinds of recycling of mantle material (Fig. 18a). The formation of oceanic crust, from melt under a mid-ocean ridge,



extracts mafic material from the mantle, and subduction then returns that material to be stirred into the mantle. While it is at the surface, in the form of oceanic crust, its complement of refractory trace elements may be modified to some degree, but will largely be retained. However its complement of noble gases will be lost, by degassing. We
⁵ may call this *external* recycling. (Hofmann has long emphasised that geochemically oceanic crust is part of the dynamic mantle system, rather than analogous to continental crust; Hofmann, 1997, 1988.) On the other hand hybrid pyroxenite, also formed by melting under a mid-ocean ridge, will recirculate *internally*. Because it does not erupt to the surface, it will not degas. Thus any complement of noble gases it has will be preserved.

It was argued in Sect. 4 that mantle heterogeneity, including subducted mafic crust and hybrid pyroxenite, will have originated early in Earth history. This implies that successive generations of both materials will have formed. As such materials are carried into a MOR melting zone, it is plausible that their melts will mix to a significant degree,

so that melt from subducted oceanic crust, previously degassed, will regain some noble gases. Some of the resulting melt mixture will erupt and degas, so that part of the complement of noble gases will be lost. The remaining melt mixture will be trapped, forming a new generation of hybrid pyroxenite that will contain the balance of the noble gases that entered the melting zone. In this way the noble gases will come to reside in the hybrid pyroxenite component of the mantle.

The initial abundances of the non-nucleogenic noble gas isotopes in the solid Earth are believed to have been one hundred to one thousand times their abundances in the present mantle (McDougall and Honda, 1998). The partial degassing process just described will have reduced this, especially early in Earth history when mantle ²⁵ convection would have been more vigorous. How much might remain can be estimated by a procedure described below. The qualitative implication at this point is that we would expect that not all of the initial noble gas complement would have been lost, and the remainder might explain the fluxes from the mantle observed at present.



Before that is addressed, there is another implication to be noted. The composition of hybrid pyroxenite will be intermediate between the compositions of the peridotite matrix and subducted oceanic crust. Because the oceanic crust is denser than average mantle through much of the depth of the mantle (Yasuda et al., 1994), so will the hybrid pyroxenite, or at least some of it. Thus we would expect some hybrid pyroxenite to settle into the D" at the base of the mantle, as does some subducted oceanic crust in numerical models (Figs. 4 and 9). Thus the D" region would accumulate a mixture of

subducted oceanic crust and hybrid pyroxenite (Fig. 18b). As described in Sect. 2, mantle plumes are expected to entrain material from the D"

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accumulations and deliver it to volcanic hotspots, at which OIBs are erupted. Thus OIBs would be expected to contain the signatures both of externally recycled, de-gassed oceanic crust and of internally recycled, gassy hybrid pyroxenite. The apparently contradictory signatures of the OIBs with the least radiogenic helium, namely depletion reflected in refractory element isotopes and a "primordial" component reflected
 in the noble gas isotopes, would thereby be accounted for.

However this does not yet explain the difference between helium in OIBs versus helium in MORBs – the different means and spreads (Fig. 16). Numerical models of recycling of oceanic crust have already demonstrated that material in the D" accumulations has a longer residence time than material circulating in the body of the mantle

- ²⁰ (Sect. 3.8). Thus we would expect that hybrid pyroxenite from D" would rise into the MOR melting zones less often, so it would degas more slowly. We could thus expect that it would have a higher content of primordial ³He than hybrid pyroxenite circulating in the body of the mantle. This could explain the higher ³He/⁴He ratios in some, but not all, OIBs.
- These qualitative conclusions can be quantified with the same approach used in Sects. 3.1 and 3.2 to estimate the fraction of remaining primitive material and the amount of subducted oceanic crust still in the mantle. In other words the evolution of noble gases can be calculated in terms of the model time, $t_{\rm m}$, relative to which convection proceeds at a steady rate. The rate of degassing is proportional to the rate of



processing through the melting zone and to the amount of gas remaining in the mantle. Thus the amount of ³He in the mantle will decline exponentially relative to model time, as in Eq. (3), though much of the ³He will reside in hybrid pyroxenite rather than in the small primitive fraction. The amount of ⁴He is determined by a competition between its generation from radioactive uranium and thorium and the same degassing process.

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An indicative calculation was presented by Davies (2010). The initial abundance of ³He was estimated by projecting exponentially backwards in time from the present abundance. The present abundances used were the "Medium gas" case of Davies (2010), shown in Table 1. Conventional estimates of noble gas abundances are based on the observed helium flux from mid-ocean ridges (Farley et al., 1995).

- are based on the observed helium flux from mid-ocean ridges (Farley et al., 1995). Several arguments indicate that actual abundances may be higher than conventional estimates. The retention of noble gases and other incompatible elements in hybrid pyroxenite would mean that only part of the mantle complement would emerge at MORs. It is argued in Sect. 6 below that conventional estimates of refractory incompatible ele-
- ¹⁵ ments are also too low, by a factor of 2–3, and the requirement to balance the masses of incompatible elements can be satisfied by such higher abundances. Ballantine at al. (2002) argue that CO₂/³He ratios and the concentrations in a so-called "popping rock" require comparably higher abundances. The "Medium" and "High" gas cases in Table 1 are obtained by increasing the He and Ne abundances by factors of 2 and
 ²⁰ 3, respectively. The High gas argon is obtained by requiring a mass balance of ⁴⁰Ar (Sect. 8 below), following Ballantine et al., and the Medium gas argon is scaled from

those values (Davies, 2010). An undegassed lower mantle case is included for comparison.

Returning to the indicative calculation of helium evolution, it is necessary to allow for a period of faster degassing within the first 0.5–1 Gyr of Earth history, which corresponds to a period of rapid mantle cooling from an initial hot state. This period of faster degassing has previously been inferred from argon observations (Allegre et al., 1987; Turner, 1989). The evolution of ⁴He is then calculated from the abundances of U and Th through time and the degassing inferred from ³He. Results are shown in Fig. 19.



The MORB curves are calculated using a residence time of 1.5 Gyr, as indicated by a numerical convection model of Davies (2008). The unradiogenic OIB curves assume a residence time 2.5 times this, which is consistent with some of the older components of the D" region in that numerical model.

⁵ The key result is that the calculated present isotopic ratios span the observed range (Fig. 16): the median MORB ³He/⁴He of about 8R_A corresponds to a ⁴He/³He ratio of about 90 000, and the least radiogenic OIB ³He/⁴He of about 35R_A corresponds to a ⁴He/³He ratio of about 20 000. The mean D" age in the Davies numerical model is about 2.5 Ga, and using this residence time in the present calculation yields a ⁴He/³He ratio of about 45 000, compared with observed median OIB ⁴He/³He ratio of about 60 000 (³He/⁴He of about 11.6R_A). The median could be readily matched by a mixture of mean D" material and MORB source material.

To be clear that this is not circular logic, the simplified degassing history, including the early faster degassing, is constrained by the need to match the present MORB isotopic ratio, but the OIB ratios are then obtained using the independent residence time estimates from a numerical convection model. Thus the MORB-source calculation demonstrates the ability of this model to accommodate the observations, and the OIBsource calculations constitute in independent test of it.

Adding confidence to these results is that fact that the observations of neon and argon isotopic ratios can be accounted for in the same calculations with no additional assumptions (Davies, 2010), although the mass balance of ⁴⁰Ar has additional uncertainties that will be discussed in Sect. 8.

The xenon isotopes ¹²⁹Xe and ¹³⁶Xe have a higher relative abundance in the mantle than in the atmosphere (McDougall and Honda, 1998), but no difference has been resolved between MORBs and OIBs, so no information about the internal structure of the mantle is implied. The ¹²⁹Xe anomaly does require some rapid early degassing of the mantle, within a few half lives of its parent ¹²⁹I (17 Myr) (Allegre et al., 1987), and this is readily accommodated by the models reviewed here.



These results indicate that the observations of noble gases in the mantle can be accommodated by the heterogeneous mantle discussed above. The gases are likely to be carried in hybrid pyroxenite. They would degas rather slowly from the mantle because they would only be partially degassed at mid-ocean ridges, the remaining gas recirculating in the hybrid pyroxenite formed from trapped melt. They would degas even more slowly from the D" accumulation because of the longer residence times of D" material. This difference in residence times is enough to account for the greater proportion of the "primordial" isotopes that is observed in ocean island basalts. Thus one of the most persistent enigmas of mantle geochemistry seems to be explainable.

10 6 Mass balances and the heat budget

A persistent argument against the mantle structure illustrated in Fig. 1, which has substantial support from geophysical observations, is that it cannot accommodate the Earth's complement of refractory incompatible trace elements nor of ⁴⁰Ar (Allegre et al., 1996, 1987; Wasserburg and DePaolo, 1979; Kellogg et al., 1999). The argument is that the amounts of these elements that are observed or inferred to be in the continental crust, the oceanic crust and the MORB source account for only about half of the amounts inferred from meteorites to be present in the Earth. Therefore an extra "enriched" or "primitive" reservoir has been invoked, presumed to be present in the deep mantle and evidently difficult to detect seismically. The "missing" portions of the elements are presumed to reside in this layer, and it is generally inferred to be quite large, comprising one-third to two-thirds of the mantle.

The earlier versions, in which the deep layer was identified with the entire lower mantle, are inconsistent with the evidence from seismic tomography that subducted lithosphere penetrates deep into the lower mantle (Grand et al., 1997), and most investigators have abandoned them. The more recent version is that the deep layer comprises about the lowest 1000 km of the lower mantle (Kellogg et al., 1999).



The difficulty with the geochemical argument is not simply that such geophysical evidence as has been offered for a deep mantle layer is not compelling (van der Hilst and Kárason, 1999). The larger difficulty is that the geophysical observations preclude much of the Earth's heat flow from coming from deeper than the source of man-

- ⁵ tle plumes, otherwise plumes would be much stronger than they are observed to be. The further implication is that much of the Earth's heat is generated *within* the MORB source. This implication is inconsistent with conventional estimates of the composition of the MORB source, which has been inferred to be strongly depleted of incompatible trace elements, including heat source elements.
- ¹⁰ Both the mass balance and the heat source arguments imply that the MORB source may not be as depleted as has been inferred hitherto, the mass balance indirectly and the heat source constraint more directly. These arguments will now be presented more explicitly. In Sect. 7 a number of reasons will then be presented why previous estimates of MORB source composition have over-estimated the degree of depletion.
- ¹⁵ It is convenient to use uranium as a representative of the refractory incompatible trace elements, in a mass balance, and as a representative of the main heat-generating elements, in a heat budget.

6.1 Uranium mass balance

Table 2 summarises estimates of uranium concentration in the Earth and in its main reservoirs (Davies, 2009b). The average U content of the primitive mantle is inferred from meteorites to be $20 \pm 4 \text{ ng g}^{-1}$, which implies a total mass of $80 \times 10^{15} \text{ kg}$ of U. (Concentrations are given as nanograms of uranium per gram of rock, rather than as "parts per billion". This removes the ambiguity of whether the ratio is by weight, volume or mole.) About (23–47) × 10^{15} kg is estimated to be in the continental crust, i.e. 30– 60%. Thus (33–57) × 10^{15} kg or 40–70% is inferred to be in the mantle.

Some of this mantle uranium we can plausibly locate in the seismic D'' zone at the bottom of the mantle. D'' is interpreted here as including accumulations of subducted oceanic crust, and the accumulation is taken, from numerical models like that of Fig. 4,



to be equivalent to a layer about 100 km thick. If its U content is similar to that of oceanic crust then it would contain only about 5% of the total U budget. This leaves about half of the Earth's U unaccounted for.

According to the mantle picture summarised in Sect. 2, the only remaining man⁵ tle reservoir is the rest of the mantle, in other words excluding the crust and the D" layer. By implication this is also the MORB source region. The balance of the Earth's uranium is then required to be in this reservoir, and Table 2 shows it would have a concentration of about 10 ± 3 ng g⁻¹. This is significantly higher than traditional estimates of 3–4.7 ng g⁻¹ (Jochum et al., 1983; Salters and Stracke, 2004; Workman and Hart, 2005). The reasons for the previous answers will be discussed in Sect. 7. Similar mass balances apply to other refractory incompatible elements.

6.2 Topographic constraint on mantle heating

At any horizontal boundary within the Earth that prevents vertical flow of material, including the core-mantle boundary, vertical heat transport must be by conduction (i.e. ¹⁵ advection is not possible). As heat conducts into the layer above the boundary it will form a thermal boundary that will be buoyant. If the rate of heat flow is sufficient (it usually will be) the thermal boundary layer will become unstable and rise buoyantly. As such a buoyant upwelling approaches the top of the surface of the Earth, its buoyancy will lift the surface, generating topography. It turns out there is a simple and direct relationship between the rate of heat flow up the upwelling and the magnitude of the topography generated at the surface (Davies, 2011, 1988a, 1999b; Sleep, 1990). A

- comparable relationship applies to topography generated by a cooling thermal boundary layer at the surface, i.e. to the seafloor subsidence caused by the cooling oceanic lithosphere (Davies, 1999b, 1988a).
- ²⁵ The manifestation of this process is sketched in Fig. 20 for two proposed mantle structures. The deep layer proposed by Kellogg et al. (1999) (Fig. 20a) would contain about half of the Earth's radioactive heat generation. This would generate strong up-wellings in the upper layer that would in turn generate substantial topography, about



half the magnitude of the mid-ocean ridge topography. On the other hand if only a little heat enters the mantle, from the core and the D'' layer, then weaker upwellings and smaller topography would result (Fig. 20b).

The only topography that can be identified with buoyant mantle upwellings is the hotspot swells. The magnitude of these swells, singly or collectively, is in no way comparable to the magnitude of the mid-ocean ridge topography, so the deep layer proposed by Kellogg et al. is incompatible with the topography of the Earth's surface.

The buoyancy implied by the various hotspot swells translates to a collective heat flow of about 3.5 TW (Davies, 1988a; Sleep, 1990). This is much less than the 30 TW associated with the cooling oceanic lithosphere and the mid-ocean ridge topography.

When the relationship between hotspot swells and plume heat flow was first pointed out it was presumed to reflect the amount of heat flowing into the base of the mantle (the inferred source of mantle plumes) from the core. More recently modelling of mantle plumes has revealed that the temperature difference between a plume and its sur-

¹⁵ roundings decreases by around 50% as the plume rises through the mantle (Labrosse, 2002; Bunge, 2005; Leng and Zhong, 2008). This implies that the heat flow also decreases as the plume rises, or in other words that the heat transported by plumes near the bottom of the mantle is about twice the amount transported near the top. Thus plumes are inferred to carry around 7 TW of heat from the bottom of the mantle. This is important for considering the mantle heat budget, as follows.

6.3 Heat budget

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The radioactive heat production implied by the above uranium budget is included in Table 2. The main heat-producing elements are uranium, thorium and potassium, and standard ratios of Th and K to U are used (Table 2). The 9 TW of heat generated in the continental crust is conducted directly to the surface, and is therefore not involved in driving the mantle. Of the heat generated within the mantle, about 90% (10 TW) is generated in the MORB source, the balance (1 TW) coming from D".



The mantle heat budget involves not only the heat generated by radioactivity but also heat flowing in from the core and heat released by the slow cooling of the mantle. Models of the thermal evolution of the core, taking account of the growth of the inner core and the energy required to generate the Earth's magnetic field, indicate a heat flow out of the core of about 5–7 TW (Davies, 2007), reasonably consistent with estimates based on seismological and other constraints (Lay et al., 2008), as is discussed in more detail by Davies (2009b). Conventional parameterised thermal evolution models of the mantle, and numerical convection models, indicate a rate of cooling of around 70 °C Gyr⁻¹, which releases 9 TW of heat (Davies, 1993). As we will see, this is not sufficient to account for the heat currently being lost from the mantle, which suggests that cooling might be faster. This possibility is discussed elsewhere (Davies, 2009a)

- that cooling might be faster. This possibility is discussed elsewhere (Davies, 2009a; see also Sect. 8 below); the following discussion would only be strengthened if it were true.
- The heat budget for the kind of mantle illustrated in Fig. 1 is shown in Fig. 21a, based on the total radiogenic heat production of 20 TW from Table 2. 6 TW is presumed to come from the core, and 1 TW of radiogenic heat is added to this in D". Plumes rise from the top of D", and therefore carry 7 TW of heat. This reduces to 3.5 TW as the plume arrives in the upper mantle, thus fitting the upper mantle heat flow inferred from hotspot swells (Davies, 1988; Sleep, 1990). Only a very small fraction of this heat leaks out through the lithosphere, and the rest is delivered to the mantle interior. The other half of the initial plume heat is lost to the mantle interior on the way up. Thus the 7 TW from the core and D" are delivered *into* the mantle. To this are added 10 TW of radiogenic heat in the mantle (Table 2) and 9 TW from cooling of the mantle, making a total of 26 TW. This amount of heat is removed from the mantle by the action of plate
- tectonics (the top boundary layer *removes* heat from the interior). In this model the MORB source is heated only 27% from below.

The effect of the deep, thick layer proposed by Kellogg et al. (1999) is illustrated in Fig. 21b. This layer was hypothesised to contain most of the incompatible elements that are not in the continental crust, so it would generate about 10 TW of radiogenic



heat. It comprises about a third of the mantle mass, so it would contribute about 3 TW from cooling. Thus a total of 19 TW would emerge through the top interface of this layer. This is where plumes would originate, so they would carry 19 TW initially. They would lose perhaps one third of their heat rising through the rest of the mantle, so delivering

- ⁵ about 12 TW to the upper mantle. This would generate topography 3–4 times larger than the observed hotspot topography. The upper two-thirds of the mantle would yield 6 TW from cooling and perhaps 2 TW of radiogenic heat, reflecting the strong depletion assumed for the MORB source. The plates would then remove the total of 27 TW from the mantle. In this model the MORB source is heated 70% from below.
- ¹⁰ Thus the observed topography of the sea floor precludes a deep layer containing a substantial fraction of the Earth's heat sources, quite apart from seismological observations, which provide no clear evidence for mantle layering. The mass balance constraint then requires the mantle's heat sources to be mainly in the MORB source, implying a uranium abundance of about 10 ng g⁻¹ (Table 2, Fig. 21a).

15 7 A mildly depleted MORB source

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The mantle structure and heat budget developed so far require a uranium content in the MORB source of about 10 ng g^{-1} , which is 2–3 times recent estimates of the U content in the so-called depleted MORB mantle: 3.2 ng g^{-1} (Workman and Hart, 2005) and 4.7 ng g^{-1} (Salters and Stracke, 2004). Because U is a typical refractory incompatible trace element, the abundances of all such elements are implied to be greater than previously inferred. The implication is that the mantle has been depleted by only about a factor of 2, from the primitive U content of 20 ng g^{-1} , rather than by a factor of 4–7, relative to primitive abundances. This implication applies to the noble gases as well as to the refractory trace elements.

²⁵ This is a significant revision of the geochemical picture of the mantle, so we need to examine why previous estimates might have been too low. There are two main reasons, each related directly or indirectly to mantle heterogeneity.



7.1 Focus on a putative "depleted" end member

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Most discussions of the MORB source composition focus on something called the depleted MORB source or the depleted mantle. To deduce its composition the discussions usually focus on something called "normal MORB". However the definition of "normal" MORB has never been clear, and it has usually been circular: "normal"

- MORB is MORB that is not abnormal (Davies, 1984). The reason is that there is no clear demarcation between "normal" MORB and "enriched" MORB or other alleged varieties, a point more recently stressed also by Hofmann (2003). The distributions of compositions are not bimodal. Rather, there is a single distribution of MORB compo-
- sition, with a long tail on the enriched side, as is suggested in Fig. 16 for strontium (histograms like this are not easy to find, a reflection perhaps of the lack of recognition of the issue). Various demarcations of normal MORB (nMORB) seem to be used, such as that it does not come from an unusually shallow ridge crest, that it does not contain an "obviously" enriched signature, that is it not too close to a hotspot, or that it is the meet common common strength of the distribution (the mede in straining terms). However, the distribution is straining of the distribution of the mede in straining terms.
- ¹⁵ most common composition of the distribution (the mode, in statistical terms). However none of these criteria prescribes a clear-cut boundary.

The problem is emphasised by Hofmann (2003) using the lanthanum/samarium ratio shown in Fig. 22. According to Hofmann nMORB is often defined as having normalised La/Sm < 1, yet this distribution is quite continuous across that value. Furthermore, an estimate of the mean concentration of La based on that criterion would be seriously in error, because it would exclude the more enriched end of the distribution in which most of the La resides.

The underlying problem here is the implicit assumption that there is a definable end member, corresponding to a definable reservoir, the "depleted MORB mantle". It is a hangover from thinking of the mantle as layered. However the geophysical evidence is inconsistent with such a conception, except for the D" region. Instead, the evidence is clear that the bulk of the mantle is heterogeneous in all respects. In that case we would expect the heterogeneity of the source to give rise to heterogeneity of MORBs, as illustrate in Fig. 7b, and as is observed.



For considering both mass balances and mantle heat generation it is the mean composition of the mantle that is important. That mean must include all components, whether they have been considered enriched, anomalous, plume-related or whatever. Because the more enriched components have been excluded from most considerations, the resulting estimates may be significantly in error, as we will see.

7.2 Chemical disequilibrium

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It was emphasised in Sect. 4 that if the mantle is heterogeneous in major elements and lithology then the bulk extraction of incompatible elements will not be governed just by local equilibrium chemical partitioning, but may be strongly affected by the va-10 garies of the migration of melts that are out of equilibrium with the peridotite matrix. As emphasised, significant quantities of melts may become trapped and remain in the residual zone from which (some) melts are extracted. Equally, such melts may not have equilibrated with their local environment so, for example, the peridotite matrix may not register their nearby presence.

- ¹⁵ Two recent estimates of the MORB-source composition (Salters and Stracke, 2004; Workman and Hart, 2005) use the composition of peridotites in key parts of their arguments. The trace element concentrations estimated by Salters and Stracke are deduced from major elements through a correlation between lutetium, a compatible trace element, and CaO in anhydrous spinel peridotites (Fig. 23). However the peridotites may not have equilibrated with the higher Lu content of eclogitic and pyroxenitic heterogeneities. Thus the Lu in the peridotites can only be regarded as a lower bound on the Lu content of the whole source. All of the other trace element concentrations in the
- analysis of Salters and Stracke are tied to the Lu content, so the trace element concentrations in the of the source would only be a lower bound.
- ²⁵ The estimate by Workman and Hart starts from the trace-element composition of clinopyroxenes from abyssal peridotites. Those peridotites likewise may not have equilibrated with enriched heterogeneities, so their estimates would also be lower bounds on the trace element content of the whole source.


It is notable that Salters and Dick (2002) found that isotopes in some MORBs from the Indian Ocean could not be explained as products of nearby abyssal peridotites, but implied an additional enriched component. They note that pyroxenites and eclogites are rare at mid-ocean ridges, though common among xenoliths and peridotite massifs, and inferred that enriched heterogeneities had been melted out of the source before

it reached the surface. In that case the residual peridotites would fail to represent the incompatible elements in those heterogeneities.

The estimates by Salters and Stracke and by Workman and Hart are also vulnerable in other respects. They both rely on equilibrium melting models for a homogeneous source, and both use long chains of inference. For example, Salters and Stracke's estimate of thorium content depends on a chain of no less than eight elemental ratios. U and K require a further ratio each. Workman and Hart begin with a reconstruction of whole-rock composition, which requires partition coefficients and modal abundances, then a melting model to estimate pre-melt composition. Both studies focus on establishing the composition of what they call the depleted mantle, to the exclusion of more enriched components. Thus both should be regarded as having established lower bounds on the trace element content of the MORB source.

7.3 Counting all components

There seem to be no relevant compilations of the mean mantle composition including all components, so some estimates must suffice here to illustrate the magnitude of the change of perspective. An indication of the effect of including most MORB values is shown in Table 3, which lists abundances of Nb, Th and U. The first row shows simple raw averages from the category "All mid-ocean ridges" from the PetDB database. The other rows show comparison values for two estimates of "normal MORB" and two enriched MORBs. U in the all-MORB average is 3–5 times larger than previous MORB estimates.

It may be that U values are less reliable because U concentrations are very low, so Th and Nb values have been included. Typical MORB ratios are Th/U = 2.6 and



Nb/U = 47 (Hofmann, 2003), so these are suitable proxies. All-MOR Th values are 2–3 times larger than previous estimates, while Nb values are 1.6–2.6 times greater. These factors may be minima, because plume-affected ridge segments may have been excluded from the "all-MOR" category of PetDB, though this is not clear from the PetDB summaries.

The role of mantle plumes also needs to be taken into account. Plumes inject material from the deep mantle, presumably including material from D", into the shallow mantle. We can hope to make some estimate of the composition of D" (as was done for Table 2), but there is no way to separate the plume material, including former D" material, that is distributed through the interior of the mantle. If we are to count all of the U that contributes to the Earth's mass balance of U, and that contributes to heating the mantle, then we must include such dispersed plume material. It turns out to comprise a surprisingly large fraction of the mantle.

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Although the heat flow carried by plumes is secondary to the heat flow associated with plate formation, the mass flow in plumes is relatively large, because the temperature difference between plumes and ambient mantle is smaller than that between subducted plates and ambient mantle. This implies that relatively more plume mass has to flow to account for the heat carried by plumes.

The rate of subduction of sea floor is 3 km² yr⁻¹ (Parsons, 1982). The strongly dif-²⁰ ferentiated part of the lithosphere is about 60 km deep, so the volume of heterogeneous lithosphere added per year to the MORB source is around 180 km³ yr⁻¹. On the other hand the volumetric flow rate of the Hawaiian plume is estimated to be about 7.5 km³ yr⁻¹ (Davies, 1992) and the Hawaiian plume carries about 10% of the global plume flow, so the global volumetric flow rate of plumes into the upper mantle is about 75 km³ yr⁻¹. This is about 40% of the plate flow, or 30% of the combined flows into the MORB source. Thus the mass flow of plumes is less than that of subducted lithosphere, but only by about a factor of about three.

Most of the plume heterogeneity will not be removed by melting, but will be stirred into the mantle (Davies, 1999b). The volumetric eruption rate of the Hawaiian plume has



been about 0.03 km³ yr⁻¹ over the past 25 Myr (Clague and Dalrymple, 1989). Even allowing for substantial subsurface emplacement of magmas, this implies that magmas represent only around 1% of the volume of the plume. If these magmas were derived by 5% melting of the plume (Hofmann and White, 1982), then only 20% of the plume would have melted, and the remainder would be stirred unaltered into the mantle.

An indication of the contribution of plume-related heterogeneities can be obtained from Table 4, which shows the enrichments of various classes of OIBs relative to conventionally-defined normal MORBs for Nb, Th and U. Hawaiian OIB is enriched by a factor of 2–3, whereas the other OIBs are enriched by factors of 10–40, with a mean of around 20. The higher enrichments are prehable due in part to relatively law meth

¹⁰ of around 20. The higher enrichments are probably due in part to relatively low melt fractions (Hofmann, 2003), so they may be upper bounds on the mean enrichments of the associated plumes.

Table 5 shows the effect of such plume enrichments on the mean composition of the MORB source, assuming plume material comprises 25% of the mantle interior (the ¹⁵ MORB source) as estimated above. If plumes are enriched by factors of 3–5 relative to the "depleted MORB mantle", then the mean mantle concentrations of incompatible elements are increased by factors of 1.5–2. Greater enrichments cannot be ruled out at this stage.

Both the compilation of "all MOR" data in Table 3 and the estimates of plume contributions in Table 5 give ample reason to suspect that the inventories of incompatible trace elements are two or more times conventional estimates. These considerations alone are potentially sufficient to account for the "missing" trace elements in the geophysically-based mantle structure of Fig. 1. There is a large data base of MORB compositions, and a more thorough analysis of it that includes all types of samples in prepartien to their likely accurrence, without arbitrary avaluations.

²⁵ proportion to their likely occurrence, without arbitrary exclusions, might yield a more reliable estimate. However any such average may still be sensitive to the smaller number of relatively enriched samples, so uncertainties will need to be carefully considered.



7.4 The melt extraction zone and the degree of melting

The degree of partial melting in the MOR melting zone has played no part in the arguments presented so far. This is in contrast to many previous considerations, in which the degree of melting is a fundamental parameter used to calculate melt composition ⁵ during equilibrium melting. Because the processes considered here involve heterogeneity and disequilibrium, the degree of melting is not easily inferred nor applied. However because the average degree of melting is often invoked, it is instructive to examine how it relates to the present picture.

A simpler way of estimating the MORB source composition than those discussed ¹⁰ in Sect. 7.2 is, conceptually, to distribute the trace element content of MORB into the melting zone, or, equivalently, to multiply MORB concentrations by the average degree of partial melting in the melt zone. This requires estimates of the size of the melting zone or of the degree of partial melting. The approaches of Salters and Stracke and Workman and Hart evidently were intended to avoid the need for such estimates, al-

though each invokes equilibrium melting models at some stage in the chain of reasoning. Moreover the simpler approach is still often invoked, at least as a rough estimate.

There are two problems with this simpler approach. First, even if the source is homogeneous there are assumptions involved that may not be commonly recognised. Second, heterogeneous melting may cause the melt extraction zone to be significantly smaller than the zone within which some melting occurs, as is clear from the earlier discussion in Sect. 4. The implicit melting models, and associated formulas, are given in Appendix A.

The result of these considerations is that this simple approach can also be misleading. In particular, with heterogeneous melting the melt extraction zone is likely to be smaller than the melting zone, and if this is not recognised then concentrations inferred from MORB will be underestimated. Thus this approach is also likely to have over-estimated the degree of depletion of the MORB source.



8 Remaining questions

8.1 The argon mass balance

The ⁴⁰Ar budget requires additional discussion. The ⁴⁰Ar abundance in the MORB source yielded by the evolution model in Sect. 5, 12 × 10¹³ atoms g⁻¹, is only 55%
of that required (22 × 10¹³ atoms g⁻¹) to balance the usual estimate of the Earth's ⁴⁰Ar budget (50 × 10¹³ atoms g⁻¹) (Davies, 2010). D" can hold only perhaps 3%. With about 50% in the atmosphere and 27% in the MORB source, this seems to leave about 20% still unaccounted for. However this deficit is much smaller than has been conventionally inferred (Allegre et al., 1996), and we should consider whether is it significant given the uncertainties involved.

The K/U ratios in both the mantle and the crust are debated, and have significant uncertainty. The mantle ratio might be lower (Albarède, 1998; Lassiter, 2004) or higher (Arevalo et al., 2009) than the value of 13000 (Jochum et al., 1983) commonly used. There may be less K in the continental crust than is usually estimated. Taylor and McLennan (Taylor and McLennan, 1985) estimated the K₂O content of the continents to be 1.1%, compared with Rudnick and Fountain's 1.9% (Rudnick and Fountain, 1995). The continental crust is so heterogeneous it is doubtful any estimates have great accuracy. If, as an illustration, we sum the mass of K in the crust using Taylor and McLennan's estimate (crustal mass 2.6×10^{25} g; K mass 2.38×10^{23} g), D" (mass 8.5×10^{25} g; K concentration 650 µg g⁻¹ and K mass 0.55×10^{23} g) and MORB source 20 (mass 390×10^{25} g; K mass 5.2×10^{23} g) we get a total of 8.1×10^{23} g of K and a bulk silicate Earth concentration of 203 μ g g⁻¹. This compares with the more usual estimate of around 240 μ g g⁻¹ (McDonough and Sun, 1995), but the total K content of the Earth has significant uncertainty because of the volatility of K during the planetary accretion process (McDonough, 2003). 25

This reduced K content $(203 \mu g g^{-1})$ would yield 169×10^{40} atoms of 40 Ar over 4.5 Gyr. The inventory for the medium gas evolution model (Sect. 5, Davies, 2010) is 48×10^{40} atoms in the MORB source and 0.7×10^{40} atoms in D". The amount in the



continental crust is not well determined but estimated to be about 7 × 10⁴⁰, and the amount in the atmosphere is 99 × 10⁴⁰ (Allegre et al., 1996). These sum to 155 × 10⁴⁰ atoms. An evolution based on the high-gas case of Table 1 yields a final total of 170 × 10⁴⁰ atoms, so between them the models span the bulk silicate amount just
 ⁵ estimated. Thus a lower crustal abundance of K, and a consequent lower global abundance of K and Ar, is consistent with the present models.

Finally, we should not really assume the Earth has retained all of its volatiles, because some of the atmosphere may have been blasted off by very large impacts during the late stages of accretion, or by the late heavy bombardment if that was a separate episode (Melosh and Vickery, 1989). Bombardment persisted until about 3.8 Ga, by which time about one third of the Earth's ⁴⁰Ar had been generated. If mantle degassing was rapid during the first 0.5 Gyr or so, then it is conceivable that the order of 10% of the Earth's ⁴⁰Ar was removed from the Earth entirely (Davies, 1999a).

Thus the ⁴⁰Ar constraint is not as stringent as has been claimed. There are un-¹⁵ certainties in the amount of potassium in the continental crust and in the bulk silicate Earth, and there may have been some early loss of ⁴⁰Ar from the atmosphere. The model presented in Sect. 5 may account for the total ⁴⁰Ar budget of the Earth when these uncertainties are allowed for.

8.2 Cosmochemical abundances and thermal evolution

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- Although the mildly-depleted MORB source mantle can resolve the mass balance and heat source questions, a remaining problem is that the abundances of heat sources (U, Th, K) inferred from cosmochemistry seem to be insufficient to allow conventional models of the thermal evolution of the mantle to match the present heat loss from the Earth's interior (Davies, 1993; Korenaga, 2008).
- ²⁵ There are three possible resolutions of this discrepancy. First, the dynamics of the mantle may be incompletely incorporated into conventional evolution models. Second, the present heat loss from the Earth may be unusually high. Third, the cosmochemical



estimates of Earth's heat sources may be too low. None of these can be ruled out at this point, so the issue remains unresolved. The three options will be discussed only briefly here.

- One version of the first possibility has been advocated by Korenaga (2006, 2008), ⁵ who argues that lithospheric plate motions are slowed by their strong resistance to bending at subduction zones, and that plate thickness was defined in the past by the dehydration accompanying melting. This would keep plate velocities and heat loss low throughout Earth history. In this scenario the mantle temperature would have peaked at very high values (1600–1700 °C) in the Archean and declined more and more rapidly ¹⁰ since, with a current cooling rate of about 150 °C Gyr⁻¹ rather than the 70 °C Gyr⁻¹
- assumed in Sect. 6.3. However Korenaga's model depends on assuming a small radius of curvature of bending plates, and this is not supported by current observations nor by recent modelling that indicates the radius of curvature will be larger for thicker plates. If even modestly more plausible radii of curvature are assumed the recent thermal
- history reverts to being close to previous conventional histories (Davies, 2009a) and the reconciliation with cosmochemical estimates is lost. It is possible that some other overlooked aspect of mantle dynamics will modify our understanding of the thermal evolution of the mantle, but no such mechanism is seems to be proposed at this time.

The second possible resolution is that the present rate of heat loss is unusually high. This would imply the mantle is cooling more rapidly than usual. This might have been true for a few hundred million years without affecting the mantle temperature too dramatically. Some fluctuations in the cooling rate are expected to have occurred just due to normal fluctuations in the age-area distribution of oceanic plates (Labrosse and Jaupart, 2007), but these may not have a large enough amplitude (Cogné and Humler, 2008), or might imply higher rather than lower heat flow in the recent past (Korenaga

2008), or might imply higher rather than lower heat flow in the recent past (Korenaga, 2007).

A more interesting possibility is that plate tectonics might have been intermittent, as suggested by Silver and Behn (2008). This would also imply that our understanding of plate motions is incomplete, though no explicit mechanism for intermittency is offered



by Silver and Behn. Intermittency would cause larger fluctuations in heat loss, and would allow the mantle to maintain its temperature over the longer term despite the present imbalance. The apparent episodicity of continental tectonics would be consistent with this, but evidence at this stage is sketchy.

⁵ The third possibility is that the cosmochemical estimates are too low. Those estimates do depend on a series of assumptions, and their uncertainty is taken by some to be about 30% (McDonough and Sun, 1995). The discrepancy of heat sources is larger than this, and it remains to be seen whether higher values might be plausible.

9 Conclusions

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¹⁰ The keys to this proposed reconciliation of mantle geochemistry with the mantle inferred from geophysical constraints and dynamical models are the rate of processing of mantle material through the mid-ocean ridge melting zones, the tendency of some subducted oceanic crust and hybrid pyroxenite to settle to the base of the mantle, the heterogeneity of the mantle at all scales and in all elements, and the effect of this heterogeneity on melting, melt migration, eruption and the distribution of incompatible elements.

The effect of source heterogeneity on melting and melt migration is quite fundamental. Old geochemical assumptions and habits of thought based on equilibrium melting of a homogeneous source may not apply. Disequilibrium seems likely down to quite small scales, and melt migration will be erratic and governed by strongly interacting physical and chemical processes.

Previous estimates of the incompatible trace element content of the mantle are likely to be lower bounds. Preliminary estimates that avoid inappropriate assumptions are not very accurate at this stage, but they indicate a clear scope for trace element contents to be several times larger than previous estimates. Sufficient data exist that better estimates can be fairly readily made.



The result, in any case, is that there are good reasons to support the claim that mass balances of incompatible trace elements can be satisfied in the geophysicallymotivated model sketched in Fig. 1. This also resolves the problem of where, in the mantle, the inferred heat-producing elements might be located. Both issues are potentially resolved if the mantle is depleted by only about a factor of 2 relative to primitive.

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The numerical modelling of Christensen and Hofmann (1994), and later extensions and refinements, have established quantitatively that refractory incompatible trace elements and their isotopes can be accommodated in the dynamic mantle. The apparentage timescale from lead isotopes is, in this interpretation, an average residence time between passages through the MOR melting zones. The differences among and between MORBs and OIBs is accounted for by the Hofmann and White hypothesis (Hof-

mann and White, 1982) that some old subducted oceanic crust settles to the D'' region, later to be brought up in mantle plumes and contribute to OIBs.

Relatively simple theoretical models of mantle sampling show that little primitive mantle should survive, they give estimates of the amount of oceanic crust in the mantle, and they explain the age distributions of mantle material yielded by numerical models. These results support and elucidate the results from numerical models of stirring by mantle convection.

The noble gases would plausibly come to reside in hybrid pyroxenite, formed when ²⁰ melt from eclogite and pyroxenite pods reacts with surrounding peridotite. A significant proportion of such melt may fail to erupt, and would recirculate in the mantle without degassing. Because it is denser than average mantle, some of the hybrid pyroxenite would settle into the D" region, where it can be tapped by mantle plumes. The amount of noble gases in MORBs and relatively unradiogenic noble gases in some OIBs can ²⁵ be quantitatively explained by this model.

It thus seems possible to reconcile the main geochemical observations of the mantle with geophysical and dynamical constraints. One main exception remains, namely the discrepancy between cosmochemical heat source abundances and the present rate of heat loss of the Earth.



Appendix A

A common expression used by geochemists (e.g. Hofmann, 2003, p. 81), who uses the equivalent concentration relationship, see below) to relate the thickness of oceanic crust, d_c , to the average melt fraction, f, in the melt zone is simply

5 $d_{\rm c} = f d_{\rm m}$

where d_m is the depth of first melting. The physical picture implicit in this formula is depicted in Fig. A1a. It is that a column of mantle material is injected vertically into the melt zone. It then partially melts, the melt segregates to the top to form the oceanic crust, and the column moves horizontally with the moving tectonic plate, thus making room for a new column to be injected. This can be called the column injection model. It is essentially a one-dimensional model of vertical injection and vertical melt segregation. It is conceptually simple but of course not physically plausible, because the sharp 90° turns in mantle flow would involve infinite energy dissipation.

A physically more plausible model, similar to that in Fig. 15a, is depicted in Fig. A1b. This model takes account of the fact that mantle flow will turn from vertical to horizontal over a finite distance, and is intrinsically two-dimensional under MORs. It also takes account of the melt flow model advocated by Spiegelman and Reynolds (1999) and discussed in Sect. 4, in which melt is drawn to the narrow eruption zone by pressure gradients in the mantle flow. The porous-medium melt flow is also intrinsically a twodimensional flow. The relationship between melt fraction and crustal thickness is a little more complicated in this case. All quantities here will be considered to be per unit length of the mid-ocean ridge (MOR). The mass of oceanic crust formed in a time δt is

$$M_{\rm c}\,=\,\rho_{\rm c}d_{\rm c}u\,\delta t$$

where ρ_c is the density of oceanic crust and u is the half spreading rate of the MOR. The mass of mantle entering the melting zone over the same time interval is

 $M_{\rm m} = \rho_{\rm m} w v \delta t$

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(A1)

(A2)

(A3)

where $\rho_{\rm m}$ is the density of the mantle and v is the ascent velocity of the mantle. The mass of melt formed will then be

 $M_{\rm melt} = f \rho_{\rm m} w v \delta t$

(A4)

(A5)

(A6)

If the extraction of melt from the melt zone into the oceanic crust is 100% efficient, then $M_{melt} = M_c$, so

 $f\rho_{\rm m}wv\delta t = \rho_{\rm c}d_{\rm c}u\delta t$

from which we derive

 $f = \rho_{\rm c} d_{\rm c} u / \rho_{\rm m} w v$

Now, if we ignore the density difference between the crust and the mantle, if v = u, and if the width of the melting zone, w, is proportional to the depth of melting, a reasonable assumption, so that $w = ad_m$, where *a* is a constant of proportionality, then

 $f = d_{\rm c}/ad_{\rm m}$

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Finally, if we know or assume that a = 1 then we recover the simple Relation (A1).

- This analysis makes it clear that Relation (A1) only applies if a number of conditions is true: the mantle ascent velocity equals the half spreading rate, the density difference between the crust and the mantle is ignored, the melt collection zone width is the same as the depth of first melting, and the melt extraction is 100% efficient. It is also possible for some of these factors to cancel others, by coincidence. Nevertheless these assumptions are not implausible if the source is homogeneous, as depicted in Fig. 15a.
- ²⁰ The uncertainties are probably similar to uncertainties in other aspects of the situation. However the simple relationship (A1) is no longer accurate if the source is heterogeneous and melting is as depicted in Fig. 15b. Figure A1c is a sketch of the relevant quantities. Now the depth of first melting is d_m , whereas the depth of peridotite melting, at which pervasive melt flow and melt "suction" begins, is d_{pm} . The width of the melt collection zone is w_{mc} , but the width of the zone over which eclogite and pyroxenite heterogeneities melt is w_m .



Suppose the melt fraction is inferred from Eq. (A1), i.e. $f = d_c/d_m$. Now suppose the concentration of an incompatible trace element in the mantle, c_m , is inferred from its concentration in the oceanic crust, c_c , from the column melting model as

 $c_{\rm m} = c_{\rm c} f = c_{\rm c} d_{\rm c} / d_{\rm m}$

⁵ If we grant the several assumptions required to reach Eq. (A6) with a = 1, then the two-dimensional homogeneous model will yield the same answer.

Now let us calculate the mantle concentration from the heterogeneous model, Fig. A1c. The mass of mantle flowing into the melt *collection* zone is now $\rho_m w_{mc} v \rho t$ and the mass of melt formed will be $f_h \rho_m w_{mc} v \delta t$, so the average melt fraction f_h in the heterogeneous case will be

 $f_{\rm h} = \rho_{\rm c} d_{\rm c} / \rho_{\rm m} w_{\rm mc}$

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If w_{mc} is considerably less than w_m (Fig. A1c) but w_{mc} is nevertheless equated to d_m , as for the homogeneous case, then we can see from this equation that f_h will be underestimated.

For example, suppose $d_c = 7 \text{ km}$ and $w_{mc} = 49 \text{ km}$. Then, ignoring density differences, $f_h = 1/7 = 0.143$. If an incompatible species has a concentration c_c in the crust, then its mantle concentration will be $c_m = f_h c_c = c_c/7$. If, on the other hand, the usual formula is used, effectively equating w_{mc} to d_m , and $d_m = 110 \text{ km}$, then the melt fraction inferred from the standard formula will be $f_s = 7/110 = 0.064$ and the inferred mantle concentration of the incompatible species will be $c_m = 0.064c_c$. This will be too low by

the factor 0.064/0.143 = 49/110 = 0.445, in other words by more than a factor of 2.

The qualitative effect of these relationships is that the crustal complement of the incompatible species is attributed to too large a mantle source volume (the melt zone instead of the melt collection zone in Fig. A1c) and so its mantle concentration is underestimated.



(A7)

(A8)

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Table 1. Noble gas abundances.

Abundances in atoms per gram. (Plausible ranges in parentheses.)						
	⁴ He (10 ¹³)	³ He (10 ⁸)	²¹ Ne (10 ⁶)	²² Ne (10 ⁸)	⁴⁰ Ar (10 ¹³)	³⁶ Ar (10 ⁸)
(a) Conventio	nal estirr	nates, MO	RB sou	rce		
Low gas	7 (5–9)	8 (6–10)	6 (4–8)	0.9 (0.6–1.1)	2 (0.5–3)	7 (2–10)
(b) New estimates, MORB source						
Medium gas High gas	14 20	16 24	12 18	1.8 3	15 22	~30? ~70?
"Undegassed lower mantle"						
Porcelli and V	Vasserbu 100	ırg (1995b 500	o) 570	150	56	600



Table 2.	Uranium	and heat	generation	budgets ^a .
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Reservoir	Mass 10 ²² kg	Mass %	U conc. ng g ⁻¹	U mass 10 ¹⁵ kg	Heat gen. ^b pW kg ⁻¹	Heat gen. TW
Average silicate						
Earth	400	100	20 ^c	80	5	20
Continental crust	2.6	0.65	1400 ^d (900–1800)	36 (23–47)	350 (225–450)	9 (6–12)
D″	8.5	2.1	50 ^e (50–80)	4 (4–7)	10.5 (10–15)	1
MORB source, i.e. rest of mantle	389	97	10 (6.5–13)	40 (26–53)	2.5 (1.5–3)	10 (7–13)

^a (Plausible ranges in parentheses.) **Bold** numbers inferred from U mass balance. 1 pW = 1 picowatt = 10^{-12} W. 1 TW = 1 terawatt = 10^{12} W.

^b Heat generation productivity from Stacey (1992), assuming Th/U = 3.8 and K/U = 13 000. ^c McDonough and Sun (1995); Lyubetskaya and Korenaga (2007); O'Neill and Palme (1998)

^d Rudnick and Fountain (1995)

^e Assumed similar to oceanic crust; Sun and McDonough (1988); Donnelly et al. (2004)

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Table 3. Average MO	RB compositions.
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	Nb	Th	U
	$\mu g g^{-1}$	ng g ⁻¹	ng g ⁻¹
"All MOR" ^a	5.95	400	240
N-MORB ^b	2.33	120	47
EPR Avg ^c	3.79	200	80
E-MORB ^b	8.3	600	180
MARK E-MORB ^c	16.05	1100	305

^a Raw averages from PetDB, www.petdb.org/

^b Sun and McDonough (1988) ^c Donnelly et al. (2004)



 Table 4. Enrichments of plume components.

Nb	Th	U
2.2	2.9	2.4
13	24	15
11	42	24
17	28	18
	Nb 2.2 13 11 17	NbTh2.22.9132411421728

Values taken from Hofmann (2003) Fig. 20. N-MORB: "normal MORB"; EM1: enriched mantle 1; EM2: enriched mantle 2; HIMU: high ²³⁸U/²⁰⁴Pb (White, 1985; Zindler and Hart, 1986).



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Table 5. MORB-source enrichments due to plume components.

Plume enrichment	MORB-source enrichment
2	1.25
3	1.5
5	2
10	3.25

Enrichment factors are relative to "depleted MORB mantle" inferred from "normal MORB". Plume material is assumed to comprise one quarter of MORB-source material (see text).



Fig. 1. Sketch of the mantle, with lithosphere and continental crust roughly to scale. The main dynamical elements of the mantle are included: subducting lithosphere and rising mantle plumes. Arrows indicate the flow associated with the plates. Chemical heterogeneity is included schematically. The D" at the bottom includes a discontinuous denser layer (black), plume feeding zone (heavy dashes) and thermal boundary layer (dotted). From Davies (1990a). Copyright Elsevier Science. Reprinted with permission.











Fig. 3. Trace element concentrations in mantle-derived rocks. Concentrations are normalised to estimated concentrations in the primitive mantle. From Hofmann (1997). Reprinted from Nature with permission. Copyright Macmillan Magazines Ltd.





Fig. 4. Temperature and streamlines (left) and tracer concentrations (right) from a numerical model with tracers that represent subducted basaltic crust that is denser than average mantle by 150 kg m^{-3} . A tracer concentration of 1 corresponds to the average basaltic content of the mantle. Red zones at the top are melted zones from which tracers have been removed to the oceanic crust. From Davies (2008): case 1 after 2000 Myr. Copyright Elsevier Science. Reprinted with permission.











Fig. 6. Neodymium isotopic composition versus latitude (degrees north) along the Mid-Atlantic Ridge. Data have been averaged over 1° intervals. ϵ (Nd) is the variation in ¹⁴³Nd/¹⁴⁴Nd, measured in parts per 10 000. From Hofmann (2003). Copyright Elsevier Science. Reprinted with permission.





Fig. 7. Contrasting conceptions of mantle sources. **(a)** Generation of a sample by mixing material from two reservoirs before eruption. **(b)** Direct sampling of a heterogeneity of intermediate composition. From Davies (2011). Copyright Cambridge University Press. Reprinted with permission.





Fig. 8. (a) Residence times from MORB and "OIB" samples of three-dimensional models (solid curves). Dashed curves are estimates based on the sampling theory (Sect. 3.9). "OIB" 50 is for an excess density of 50 kg m^{-3} , "OIB" 100 is for 100 kg m^{-3} . (The "OIB" interpretation is discussed below.) **(b)** Final residence time as a function of processing time, τ . Curves are from the sampling theory (Sect. 3.9) for simple sampling (solid) and two cases in which a sampling delay has been assumed (400 Myr, dashed; 1.2 Gyr, dash-dot). Results from various numerical models are indicated by the symbols. From Huang and Davies (2007b, a). Copyright American Geophysical Union.





Fig. 9. Cut-away images of **(a)** temperature and **(b)** tracer concentration in a three-dimensional spherical model of mantle stirring with heavy tracers. After Huang and Davies (2007b). Copyright American Geophysical Union.





Fig. 10. Histogram of MORB tracer ages (black) compared with the age distribution predicted from the simple sampling theory (solid grey) and with a sampling delay time of 0.4 Gyr (Earth time; dashed grey). The tracer ages are given relative to the final model time. After Huang and Davies (2007a). Copyright American Geophysical Union.





Fig. 11. Images from the three-dimensional regional model of Huang and Davies (2007c). **(a)** Temperature after 200 Myr of model time, **(b)** tracer concentration after 18 Gyr of model time.




Fig. 12. Analysis of results from the model of Fig. 11. (a) Cumulative percentage of processed tracers (blue), (b) ages of MORB (blue) and OIB (red) samples. Both plots include the result from the sampling theory with variable processing time (magenta, dashed), and from the theory using constant process times: the initial processing time of 1.98 Gyr (green, dashed) and the final processing time of 4.23 Gyr (green, solid). The dash-dot line in (a) is the amount of degassing of ⁴⁰Ar relative to the total amount produced by the decay of ⁴⁰K.





Fig. 13. Solidi (lower) and liquidi (upper) for an average mantle composition (pyrolite) and for eclogite, the upper mantle form of subducted ocean crust. An approximate solid adiabat is included. After Yasuda et al. (1994). Copyright American Geophysical Union.





Eclogite body
Melt channel
+ reaction zone
Streamlines

Fig. 14. Sketch of the migration of melt emerging from eclogite bodies. The melt will react with surrounding peridotite, and will tend to refreeze. Some might react completely and become trapped in the mantle, whereas other melt might migrate a significant distance and reach the peridotite melting zone. Curves suggest streamlines of the mantle flow. After Davies (2009b). Copyright American Geophysical Union.





Fig. 15. Sketches of melting under a mid-ocean ridge. **(a)** Assuming a homogeneous source. The curves are flow lines of the solid mantle. **(b)** Assuming a heterogeneous source. Old subducted oceanic crust (Old MORB) in the eclogite assemblage will start melting at a greater depth than peridotite. Some of the resulting melt may fail to be extracted, and remain as hybrid pyroxenite. Multiple generations of hybrid pyroxenite may return to the melting zone. After Davies (2009b). Copyright American Geophysical Union.







Fig. 16. Histograms of isotopic ratios observed in MORB (green) and OIB (yellow). Helium is normalised to the atmospheric ratio, $R_A = 1.4 \times 10^{-6}$. Dashed lines mark \pm one standard deviation about the medians (solid lines). ³He/⁴He values for MORB and OIB are 7.92 \pm 1.06 R_A and 11.62 \pm 5.82 R_A , respectively; ⁸⁷Sr/⁸⁶Sr values are 0.7026 \pm 0.0004 and 0.7036 \pm 0.0010; ²⁰⁶Pb/²⁰⁴Pb values are 18.32 \pm 0.39 and 19.16 \pm 0.77. After Ito and Mahoney (2006). Copyright American Geophysical Union.



Fig. 17. Nd-Pb-He isotopes of OIB and MORB. High ³He/⁴He OIB have the most MORB-like Nd and the lowest Pb isotope ratios. From Class and Goldstein (2005). Reprinted from Nature with permission. Copyright Macmillan Magazines Ltd.





Fig. 18. Recycling through the mantle. **(a)** formation of oceanic crust, which degasses, and formation of hybrid pyroxenite, which does not degas. **(b)** Both old subducted oceanic crust and hybrid pyroxenite are denser than average mantle and would tend to accumulate in the D'' region, where they might be sampled by mantle plumes.





Fig. 19. An indicative calculated evolution of helium isotope concentrations and ratios. MORB source: solid curves; unradiogenic OIB source: short-dashed; radiogenic production: long-dashed. The degassing rate is assumed to have been 3 times higher during the first 0.5 Gyr. Dark grey: observed MORB range; light grey: observed OIB range. The MORB source calculation assumes a residence time of about 1.5 Gyr, whereas the unradiogenic OIB source residence time is assumed to be 2.5 times greater, i.e. about 3.75 Gyr. From Davies (2010). Copyright American Geophysical Union.





Fig. 20. Sketches of relationship between heating and topography. (a) A thick lower layer supplies strong heating to the base of the upper layer, generating a strong buoyant upwelling and large topography. (b) A thin layer supplies only a small amount of heat, generating a weaker upwelling and small topography.

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Interactive Discussion



Fig. 21. Heat budgets of alternative mantle models. **(a)** Preferred model: thin D" region and a mildly depleted MORB source comprising most of the mantle. **(b)** Deep mantle layer containing about half of the Earth's refractory incompatible elements. Only **(a)** is consistent with observed hotspot swells. See text for details.





Fig. 22. La/Sm versus La, normalised to primitive-mantle, for MORB from three Ocean basins. Lanthanum concentrations vary by about two orders of magnitude; La/Sm varies by more than one order of magnitude. Data were extracted from PETDB. From Hofmann (2003). Copyright Elsevier Science. Reprinted with permission.





Fig. 23. Lu variations with CaO in anhydrous spinel peridotites. Mantle Lu is inferred assuming 3.50 wt% CaO for the depleted mantle. From Salters and Stracke (2004). Copyright American Geophysical Union.







Fig. A1. Physical models of melting implicit in various formulae. **(a)** The column injection model implicit in the common formula relating melt fraction to thickness of oceanic crust. **(b)** A more realistic depiction of melting relationships in a homogeneous source, similar to Fig. 15a, involving two-dimensional flows of both the mantle and melt. **(c)** A depiction of melting relationships for a heterogeneous source, similar to Fig. 15b.