

Numerical models, geochemistry and the zero-paradox noble-gas mantle

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Published online 1 October 2002

Numerical models of whole-mantle convection demonstrate that degassing of the mantle is an inefficient process, resulting in *ca.* 50% of the ⁴⁰Ar being degassed from the mantle system. In this sense the numerical simulations are consistent with the ⁴⁰Ar mass balance between the atmosphere and mantle reservoir. These models, however, are unable to preserve the large-scale heterogeneity predicted by models invoking geochemical layering of the mantle system. We show that the three most important noble-gas constraints on the geochemically layered mantle are entirely dependent on the ³He concentration of the convecting mantle derived from the ³He flux into the oceans and the average ocean-crust generation rate. A factor of 3.5 increase in the convecting-mantle noble-gas concentration removes all requirements for: a ³He flux into the upper mantle from a deeper high ³He source; a boundary in the mantle capable of separating heat from helium; and a substantial deep-mantle reservoir to contain a hidden ⁴⁰Ar rich reservoir. We call this model concentration for the convecting mantle the ‘zero-paradox’ concentration.

The time-integrated flux of ³He into the oceans is a robust observation, but only representative of the ocean-floor activity over the last 1000 years. In contrast, ocean-floor generation occurs over tens of millions of years. We argue that combining these two observations to obtain the ³He concentration of the mantle beneath mid-ocean ridges is unsound. Other indicators of mantle ³He concentration suggest that the real value may be at least a factor of two higher. As the zero-paradox concentration is approached, the noble-gas requirement for mantle layering is removed. We further consider the role that recycled material plays in ocean-island-basalt generation and show that a source with high ³He and ³He/⁴He must exist within the mantle. Nevertheless, only a small amount of this material is required to generate both the

One contribution of 14 to a Discussion Meeting ‘Chemical reservoirs and convection in the Earth’s mantle’.

observed ocean-island $^3\text{He}/^4\text{He}$ ratios and the concentrations inferred from basalt samples for this mantle source.

Keywords: helium; flux; whole mantle; layering;
mid-ocean-ridge basalts; ocean-island basalts

1. Introduction

The continuing interplay between the processes of chemical differentiation at the Earth's near surface and the dynamics of mixing in the mantle system variably work to create and destroy the geochemical record of the Earth's past. Two apparently incompatible conceptual models of whole-Earth behaviour have been championed by different sections of the Earth Sciences. The geochemical community has favoured a layered model of the mantle, in which a shallow well-mixed, volatile-poor and depleted reservoir supplies mid-ocean-ridge volcanism. In this model, plumes feed intraplate volcanism from the deep mantle and sample a more volatile-rich and less depleted portion of the mantle. The boundary between these reservoirs has often been assumed to be at a depth of 670 km, where either a chemical boundary or the endothermic phase change from spinel to perovskite/magnesiowüstite structure in the mantle has been assumed to have prevented large-scale mass transfer and mixing. In contrast, the geophysical community has, with a few notable exceptions, favoured a mantle in which subducting slabs and related convection result in significant mass transfer across the 670 km discontinuity.

Although early seismological inferences of slab subduction failed to convince the geochemical community that significant mass transfer between upper- and lower-mantle regions occurs (e.g. Dziewonski 1984; Creager & Jordan 1986; Grand 1987), more recent tomographic evidence for both slab subduction (Grand 1994; van der Hilst *et al.* 1997) and plume penetration (Bijwaard & Spakman 1999; Goes *et al.* 1999) through the 670 km discontinuity is now overwhelming. This remains at odds with several key geochemical observations requiring that significant reservoirs preserve chemical heterogeneity in the mantle for billions of years. Full recent reviews on the impact these observations have had on geochemical models can be found in van Keken *et al.* (2002) and Porcelli & Ballentine (2002).

In this paper, we briefly review the geochemical observations that resulted in the formation of the layered-mantle concept, before focusing on the noble-gas evidence. Noble gases have played a key role in the geochemical arguments for mantle layering because of their chemical inertness, high volatility and low concentration. The latter enables small additions from natural radioactive decay of U, Th and K to significantly alter the noble-gas isotopic-abundance pattern. This in turn enables a temporal link between these radioelements and the mantle volatile concentration to be derived. Specifically, we examine the following three aspects of the noble-gas armoury:

- (1) the $^3\text{He}/^4\text{He}$ -ratio difference between mid-ocean-ridge volcanism and oceanic-island volcanism and the arguments for mass transfer between these reservoirs;
- (2) the ^{40}Ar mass balance and the requirement for a large and deep ^{40}Ar -rich reservoir; and
- (3) the relationship between heat and helium used to argue for a deep-mantle boundary layer in the mantle able to decouple these related observables.

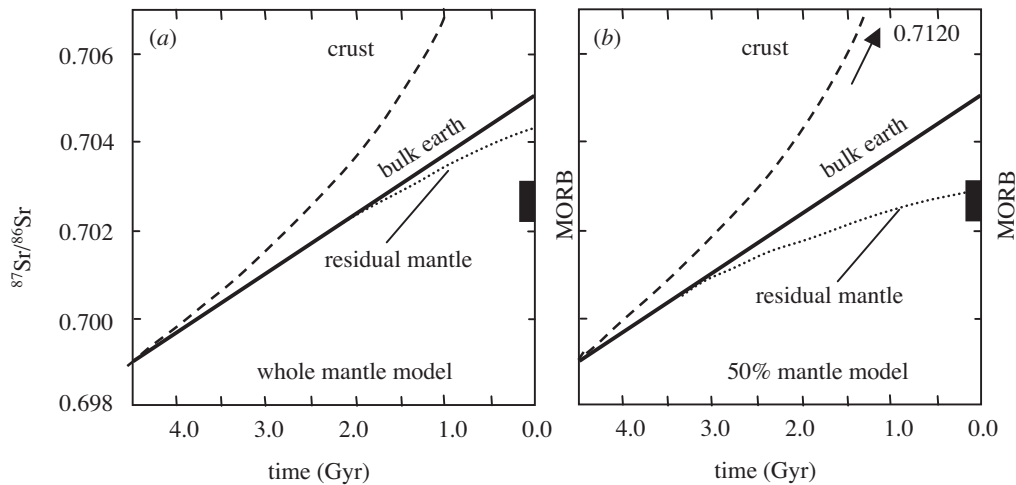


Figure 1. The Sr-isotope evolution of the continental crust and residual mantle for a simple two-stage model of mantle depletion. The Rb/Sr parent–daughter ratio is not reduced sufficiently in the residual mantle to give the observed mantle (MORB) Sr-isotopic composition if depletion occurred from the whole mantle (a). Crust formation from 50% of the mantle only (b), however, gives the observed isotopic composition. A similar approach was applied to show that a 30–50% mantle model could account for K, Ar, Rb, Sr, Sm, Nd, U, Th and Pb abundances and Sr, Nd and Pb isotopes (Jacobsen & Wasserburg 1979; De Paolo 1980; O’Nions *et al.* 1979).

Finally, we discuss a key discrepancy between predicted and measured noble-gas concentrations in ocean-island basalts (OIBs).

2. Development of the geochemical layered-mantle model

Early two-stage models of crustal growth, parent/daughter mass balance and mantle differentiation noted that the difference between the isotopic composition of the crust and the mantle could only be explained if the volume of the mantle that had been depleted was between 30 and 50% of the whole mantle volume (figure 1). This simple model accounted for a wide array of trace elements and isotopic pairs, including K, Ar, Rb, Sr, Sm, Nd, U, Th and Pb abundances as well as Sr, Nd and Pb isotopes (Jacobsen & Wasserburg 1979; De Paolo 1980; O’Nions *et al.* 1979). Although the nature of the seismic discontinuity at a depth of 670 km in the mantle was still being explored, either a composition change or a strong endothermic phase change was expected to impede mass transfer across this boundary and volumetrically divide the mantle into two regions roughly compatible with the geochemical mass balance. These foundations firmly established the geochemical division of the mantle into ‘upper’ and ‘lower’ mantle reservoirs, which today are explicit or implicit at some level in almost all geochemical papers to date addressing the chemical and isotopic evolution of the mantle system.

An important conceptual step was the development by Galer & O’Nions (1985) of a model in which limited mass transfer between the lower mantle and upper mantle occurred. These workers noted that the present-day U/Th ratio in the ‘upper’ mantle recorded by Th isotopes was lower than the time-integrated U/Th ratio recorded by

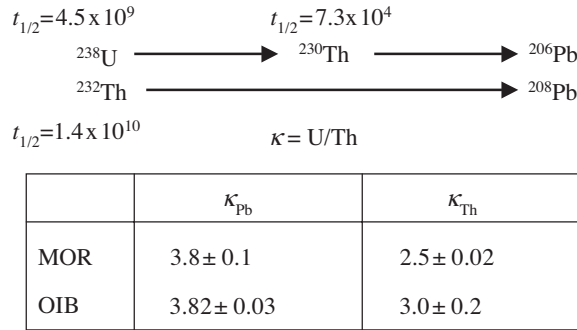


Figure 2. Steady-state Pb mantle. The $^{238}\text{U}/^{232}\text{Th}$ ratio in basalt (κ) cannot be measured directly because of elemental fractionation on eruption. ^{230}Th is a decay product of ^{238}U and can be used indirectly to obtain a $^{238}\text{U}/^{232}\text{Th}$ ratio (κ_{Th}). Because of the short ^{230}Th half-life, this ratio is representative of the present-day source value. In contrast both U and Th decay to different Pb isotopes. The Pb-isotopic ratio can also be used to calculate the $^{238}\text{U}/^{232}\text{Th}$ ratio (κ_{Pb}) but, because of the long half-lives of ^{238}U and ^{232}Th , this value represents a time-integrated value. Differences between the present-day and time-integrated $^{238}\text{U}/^{232}\text{Th}$ ratio for the upper mantle have been explained by a flux of material from the lower mantle, and a limited residence time of Pb in the upper mantle (Galer & O’Nions 1985).

the Pb-isotope system, which in turn was the same as that found in ocean-island basalts sampling the ‘lower’ mantle (figure 2). In their model this could be explained if Pb from the ‘lower’ mantle was fluxed into the ‘upper’ mantle but did not reside in this reservoir long enough to develop a signature of the actual U/Th ratio. The residence time of the Pb in the upper mantle was estimated to be *ca.* 600 Myr.

Nevertheless, the early models considered neither complicated scenarios of crustal evolution (Taylor & McLennan 1995; Armstrong 1991), nor the possibility of recycling of material with different functional inputs into different mantle reservoirs, which can account for many of these observations without placing stringent mass-balance constraints on specific reservoirs within the mantle (Kramers & Tolstikhin 1997; Elliott *et al.* 1999; Hofmann 1997).

3. Noble gases and the layered mantle

The greatest strength of using noble gases as tracers of mantle processes is their chemical inertness and volatility. These characteristics result in efficient outgassing of the noble gases during melting, with negligible recycling back into the mantle system, which greatly simplifies their interpretation. This is particularly true for He, which, once degassed from the mantle or crust, has a residence time in the atmosphere of *ca.* 1 Myr, before being lost to space (Allègre *et al.* 1986; Torgersen 1989). For the other noble gases, such as Ar, the atmosphere becomes their final resting place. The other important feature of noble gases is that they are highly depleted in the Earth relative to solar abundances. This results in small noble-gas additions from U, Th and K decay-related products being readily resolvable. For example, ^4He is produced by U and Th decay chains and alters the $^3\text{He}/^4\text{He}$ ratio trapped in the mantle during accretion. Volcanic products with different $^3\text{He}/^4\text{He}$ must therefore reflect mantle sources or reservoirs with different $^3\text{He}/(\text{U}+\text{Th})$ ratios. The observation that mid-ocean ridges have a $^3\text{He}/^4\text{He}$ ratio of $8Ra$ (where $Ra = 1.4 \times 10^{-6}$ and is the $^3\text{He}/^4\text{He}$

ratio in the atmosphere) compared with higher values in some OIBs, up to $38Ra$, provides very clear evidence that these systems sample different mantle reservoirs, and indeed is entirely consistent with the layered-mantle concept (Kurz *et al.* 1982; Allègre *et al.* 1986).

The very low concentration of ^3He in the atmosphere and oceans results in small magmatic additions to sea water being readily resolvable (Clarke *et al.* 1969). Given the mean residence time of volatiles in the ocean (1000 yr) and corrections for variations in the ocean-circulation pattern, an estimate of the mantle ^3He flux into the oceans can be derived (1060 mol ^3He per year; see Lupton & Craig (1975) and Farley *et al.* (1995)). The rate of ocean-plate generation is estimated at $20 \text{ km}^3 \text{ yr}^{-1}$ (Parsons 1981). Partial melting of the mantle source to produce mid-ocean-ridge basalt (MORB) is taken to be 10% (Langmuir *et al.* 1992). Combined, these observations give the ^3He concentration in the mantle beneath mid-ocean ridges as 1.18×10^9 atoms ^3He per gram. We can then calculate the effect of U and Th decay in a closed system with this ^3He concentration. Taking the initial $^3\text{He}/^4\text{He}$ ratio of the mantle to be the pre-deuterium-burning solar value of $120Ra$, 0.07×10^{14} atoms ^4He per gram then have a trapped accretional origin (often called primitive or primordial). The mantle supplying mid-ocean ridges has U and Th concentrations of 0.008 ppm and 0.016 ppm, respectively (Jochum *et al.* 1983). In 4.5 Gyr these radioelements would produce 3.12×10^{14} atoms ^4He per gram. Assuming negligible ^3He production (the radiogenic $^3\text{He}/^4\text{He}$ production ratio is around 1×10^{-8}), a closed-system $^3\text{He}/^4\text{He}$ ratio for the mantle beneath mid-ocean ridges would therefore be $2.6Ra$. This is considerably more radiogenic than the observed value of $^3\text{He}/^4\text{He} = 8Ra$. A simple explanation for this difference is a flux of a high $^3\text{He}/^4\text{He}$ component into the mantle supplying mid-ocean ridge volcanism. The observed high $^3\text{He}/^4\text{He}$ in ocean-island volcanism provides the evidence for this reservoir and forms one foundation for the two-layered-mantle model.

Earlier work considered the possibility that this high $^3\text{He}/^4\text{He}$ flux may be in the form of a steady-state diffusive flux of ^3He across a boundary layer in the mantle, taken to be the 670 km discontinuity (O'Nions & Oxburgh 1983; Allègre *et al.* 1986). Following the approach of Galer & O'Nions (1985), Kellogg & Wasserburg (1990) developed a similar steady-state model for He, in which a small mass flux from the lower mantle supplied high $^3\text{He}/^4\text{He}$ into the upper or mid-ocean-ridge source mantle. In low-enough concentrations, the ^4He produced in the upper mantle by U and Th would lower the $^3\text{He}/^4\text{He}$ ratio to the value observed, given a ^3He residence time in the upper mantle of *ca.* 1.4 Gyr. Significant advances in understanding the noble-gas-isotopic composition of heavier noble gases in MORBs and OIBs (Sarda *et al.* 1988; Staudacher *et al.* 1989; Honda *et al.* 1991; Poreda & Farley 1992) enabled this approach to be extended first to Ne and Ar (O'Nions & Tolstikhin 1994) and finally a complete formulation for He, Ne, Ar, Kr and Xe that includes consideration of a return or subduction flux (Porcelli & Wasserburg 1995*a, b*).

The ^{40}Ar mass balance is also intrinsically linked to the ^3He concentration in the upper mantle, estimated from the ocean- ^3He flux. With an upper-mantle $^3\text{He}/^4\text{He} = 8Ra$ and a source concentration of 1.18×10^9 atoms ^3He per gram, the ^4He concentration in the upper mantle is 1.05×10^{14} atoms ^4He per gram. Of this, 0.98×10^{14} atoms ^4He per gram are due to the radioactive decay of U and Th. Taking $K/U = 12\,500$ (Jochum *et al.* 1983) and closed-system decay over 4.5 Gyr, the relationship between ^4He and ^{40}Ar is established, where $^4\text{He}/^{40}\text{Ar}(4.5 \text{ Gyr}) = 1.55$,

giving an upper-mantle ^{40}Ar concentration of 0.63×10^{14} atoms ^{40}Ar per gram. Taking the mass of the upper mantle to be 1.34×10^{27} g leads to a total ^{40}Ar content of the upper mantle of 8.44×10^{40} atoms ^{40}Ar .

The amount of ^{40}Ar in the upper mantle can be compared with the total amount of ^{40}Ar produced by K decay. Taking a bulk silicate Earth (BSE) K content of 240 ppm (McDonough & Sun 1995) combined with the mass of the silicate Earth (4.032×10^{27} g) gives 1.94×10^{42} atoms ^{40}Ar produced over 4.5 Gyr. The ^{40}Ar derived from K decay now in the atmosphere is 0.992×10^{42} atoms ^{40}Ar (Ozima & Podosek 1983). The difference between the total amount of ^{40}Ar produced and that now in the atmosphere is accommodated neither in the upper mantle, nor in the whole mantle at the same low concentrations. This discrepancy is the underlying argument for a deep mantle with significantly higher concentrations of ^{40}Ar than current upper-mantle estimates. This has become one of the central features of papers advocating a geochemically layered mantle (Allègre *et al.* 1996).

^4He and heat are both produced by U and Th decay in the mantle at a constant ratio. Their respective flux from the mantle has also played an important role in the development of the layered-mantle model (O’Nions & Oxburgh 1983). The ^4He flux is directly linked to the ^3He flux measured in the oceans, given an upper-mantle $^3\text{He}/^4\text{He}$ of $8Ra$. O’Nions & Oxburgh (1983) observed almost an order of magnitude more heat than ^4He escaping from the mantle than would be expected given their interrelationship. These workers argued that the extraction of heat and He from the Earth near the surface would not cause preferential retention of He in the mantle because of the incompatible nature of He during melting. Instead, they argued that a deeper boundary layer existed in the Earth’s mantle, through which heat but not He could efficiently escape. The ^4He production in the upper mantle with U = 0.008 ppm and Th = 0.016 ppm matches the observed flux, providing supporting evidence for the mantle phase change at a depth of 670 km being the postulated boundary.

All three noble-gas constraints on layering within the mantle are inexorably bound to the upper-mantle He concentration derived from the measured ^3He flux into the oceans.

4. Numerical models of mantle convection

Recent advances in high-resolution seismic tomography and their impact on our understanding of mantle convection, plume origin and preservation of mantle heterogeneity (Bijwaard & Spakman 1999; Goes *et al.* 1999; Grand 1994; van der Hilst *et al.* 1997; van der Voo *et al.* 1999; Kaneshima & Helffrich 1999) have been complemented by advances in numerical models simulating mantle convection. Numerical models have, over the last decade, seen a dramatic change in the level of resolution and model sophistication due to the availability of ever increasing computer resources. The earliest models were typically two-dimensional (2D) Cartesian boxes, bottom heated with arbitrary interfaces imposed as boundary conditions to investigate the effect of whole-box versus layered-box convection with some Earth-like parameters (e.g. McKenzie & Richter 1981; Gurnis & Davies 1986). Because of limited computer resources, a low-resolution system was typically employed in this earlier work, requiring scaling from low thermal buoyancy and boundary forces (Rayleigh number and Péclet number, respectively) to more Earth-like values. Reviews by Silver *et al.* (1988), Kellogg (1992) and Schubert (1992) detail most of this earlier work.

More recently, the emphasis in model development has focused on improved geometry and resolution and the incorporation of more and better-defined ‘Earth-like’ parameters. These parameters include a suitably scaled combination of bottom heating and internal heating, attempts to model the rheology as a function of pressure and temperature, the addition of phase changes with appropriate Clapyron slopes, the choice of convection parameters that reproduce the observed heat flow, an investigation of density contrasts and and attempts to provide ‘self-consistent’ plate behaviour.

The development of curvilinear geometry in models has enabled the effect of asymmetry on mixing between the upper and lower thermal boundary layers to be included in the fluid-dynamics regime in both 2D and 3D models. For example, the resulting 2D cylindrical models reflect more that the outer boundary has a larger surface area than the lower boundary and avoids distortion at the edge of the Cartesian box (Jarvis 1993). Schmalzl *et al.* (1996) investigated the differences between 2D and 3D mixing in isoviscous mantle-convection models at comparable convective vigour. They argued for significant differences in mixing behaviour and in particular that mixing in three dimensions was less efficient than in two dimensions. It should be noted that these experiments were limited to poloidal flow only. Ferrachat & Ricard (1998) and van Keken & Zhong (1999) show that 3D mixing is in fact more efficient due to the effect of toroidal flow. Van Keken & Zhong (1999) note that, within some areas, regular ‘islands’ of laminar stretching persist, in which unmixed material can survive. With temporally evolving surface boundary conditions constrained by observed plate motion, these ‘islands’ will be rapidly mixed back into the larger convective system (van Keken & Zhong 1999). While the incorporation of plates in numerical models clearly provides a critical element with respect to their mixing behaviour, numerical models do not yet have the capability to generate self consistent ‘Earth-like’ plate behaviour, although significant advances have been made (Tackley 1998; Trompert & Hansen 1998).

Although the ideal goal of high-resolution full 3D convective systems with Earth-like parameters and self consistent plates has not yet been achieved, careful formulations of 2D-cylindrical models are providing important information about the behaviour of the mantle system.

5. Noble gases and models of mantle convection

In particular, the incorporation of noble-gas geochemistry into numerical models has provided an important insight into the efficiency of mixing and degassing and the role of phase change and viscosity on these processes. Van Keken & Ballentine (1998, 1999) considered 2D cylindrical models that match the convective vigour of the present-day Earth, as measured by surface heat flow and plate velocity. Passive tracers contain information about U, Th, ^3He , and ^4He concentrations. With time, U and Th decay to ^4He and reduce the $^3\text{He}/^4\text{He}$ ratio. Tracers that pass through mid-ocean-ridge analogues were ‘degassed’ by reducing the He concentration to close to zero. The continuing decay of U and Th to ^4He builds up a radiogenic ^4He concentration within these tracers. In this manner the $^3\text{He}/^4\text{He}$ evolution and distribution within the model mantle was investigated. The first investigation was a test of the hypothesis that a high-viscosity lower mantle alone could preserve large-scale geochemical heterogeneity (van Keken & Ballentine 1998). The second investigation

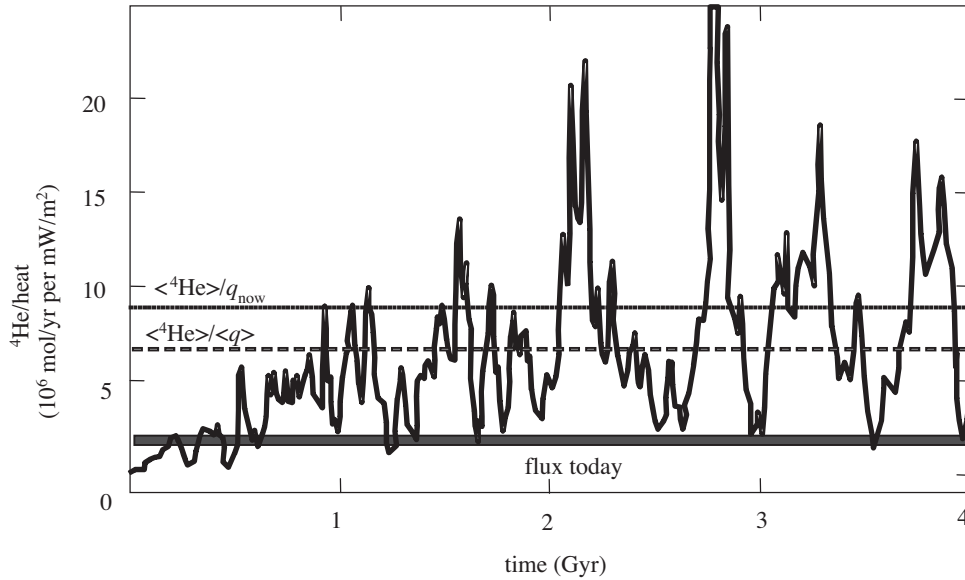


Figure 3. ${}^4\text{He}/\text{heat}$ variation with time generated by a numerical model simulating whole-mantle convection (after van Keken *et al.* 2001) shows that large temporal variations in ${}^4\text{He}/\text{heat}$ occur. Nevertheless, ${}^4\text{He}/\text{heat}$ values as low as the values observed are infrequent and are of relatively short duration. Running average: 50 steps (20 Myr).

included the role of phase change and a pressure- and temperature-dependent rheology (van Keken & Ballentine 1999). Both approaches failed to preserve a substantial high- ${}^3\text{He}/{}^4\text{He}$ and poorly mixed reservoir that could provide the source for observed ocean-island volcanism. The principal conclusion of this work was that neither the high viscosity of the lower mantle nor the phase change at a depth of 670 km, either alone or together, could prevent efficient mixing of the whole-mantle system over the time-scale of the Earth.

Another advantage of this numerical-modelling approach is that unrealistic parameters, such as a higher than accepted buoyancy effect of the phase change at a depth of 670 km, can be investigated. This is useful to investigate the consequences of systems that have been proposed in conceptual form, but not dynamically tested, by forcing some degree of layering (either meta-stable or stable). For example, models were investigated that induced layering followed by overturn to assess the viability of models advocating that the mantle has recently changed its convective mode (e.g. Allègre 1997). Meta-stable numerical models show partial development of layering followed by rapid mantle overturn resulting initially in a lower mantle with a more radiogenic ${}^3\text{He}/{}^4\text{He}$ than the upper mantle. This is the opposite of the observed difference between ${}^3\text{He}/{}^4\text{He}$ at ocean islands and at mid-ocean ridges. A further consequence is that the temperature of material reaching the surface shortly after overturn is far higher than ambient upper mantle. While the geological record is limited, there is no evidence of major episodic variations in the upper-mantle temperature (Abbott *et al.* 1993; Galer & Mezger 1998). Upon overturn, mixing is rapid and within a few hundreds of Myr the large-scale isotope inversion is reduced to the small-scale heterogeneity observed in models with more Earth-like phase-change values (van Keken & Ballentine 1999). Models with extreme phase-change values can

of course generate stable layering. By design this recreates the geochemical cartoon, but the consequences are several fold:

- (i) no subduction occurs through the 670 km phase change;
- (ii) no plumes cross the 670 km phase change;
- (iii) there is a very large thermal boundary at 670 km; and
- (iv) the higher temperature of the lower mantle in the P, T -dependent rheology of the model results in a lower-mantle viscosity similar to that of the upper mantle.

Such consequences demonstrate that models invoking a mantle layered at a depth of 670 km by phase change and/or viscosity, either now or in the past, are untenable (van Keken & Ballentine 1999).

It is important to note that the efficiency of degassing of radiogenic ^4He (or ^{40}Ar in later work) in the most Earth-like models are of the order of *ca.* 50%. This is indistinguishable from the efficiency of outgassing of ^{40}Ar , calculated from the terrestrial ^{40}Ar mass balance. Layering of the mantle is not necessary to isolate the missing ^{40}Ar . Within a regime of whole-mantle convection this occurs simply as a feature of degassing efficiency. One consequence of such a scenario, however, would be that the average upper-mantle ^{40}Ar concentration would have to be significantly higher than current estimates based on the ^3He flux into the oceans.

A natural progression of this approach has been the study of the $^4\text{He}/\text{heat}$ variance produced by these dynamical models (van Keken *et al.* 2001). Unlike steady-state or box-modelling approaches, the variation in $^4\text{He}/\text{heat}$ at the model surface is a function of both extraction mechanism (degassing at the mid-ocean ridge analogue in the case of He and a uniform surface extraction function for heat) and fluid-dynamics controlled $^4\text{He}/\text{heat}$ heterogeneity. Improvements in the model used over earlier versions include the addition of K and its decay to ^{40}Ar and the introduction of secular cooling in the model that is directly linked to the U, Th and K heat production. The hypothesis tested was simply whether or not an episodically reduced $^4\text{He}/\text{heat}$ ratio was a natural product of differential extraction in a regime of whole-mantle convection.

Figure 3 shows the results of the model $^4\text{He}/\text{heat}$ variance as a function of time (van Keken *et al.* 2001). At the start of the model, a large amount of heat is produced, but U decay has not yet produced high concentrations of ^4He in the mantle, resulting in low initial $^4\text{He}/\text{heat}$ ratios. As the model progresses, ^4He ingrowth and degassing become significant and a large amount of variance in the $^4\text{He}/\text{heat}$ about the mantle mean is observed. Three times within the last 10^{-12} yr of the model, the model $^4\text{He}/\text{heat}$ drops to values similar to those observed. Nevertheless, these excursions to low $^4\text{He}/\text{heat}$ occur infrequently and only for relatively short periods of time. Notwithstanding the argument that we may be ‘living in special times’, the conclusion was that the $^4\text{He}/\text{heat}$ imbalance remains evidence for a boundary layer within the Earth capable of separating heat from helium. An implicit consequence is that the noble-gas concentration within the upper mantle is reasonably well represented by the ^3He flux and ocean-crust generation rates discussed in §1. We now assess this supposition in more detail.

An important point to note is that the time resolution of the numerical model investigating $^4\text{He}/\text{heat}$ variance (van Keken *et al.* 2001) is *ca.* 4×10^5 yr. The additional statistical fluctuations in the tracer density result in high-frequency ^4He flux variation. To smooth the resolution-induced noise and to assess the first-order dynamical effects, the $^4\text{He}/\text{heat}$ ratio has been smoothed in the study by van Keken *et al.* (2001) by taking a running average over 50 time-steps, or 20 Myr. This is far in excess of the 1000 yr residence time of the ^3He flux record in the oceans today. Furthermore, the numerical model does not address near-surface processes of extraction such as melt generation, migration, magma-chamber formation, eruption or on-/off-axis hydrothermal activity. These processes all share the potential to separate the heat flux from helium. For example, on a site-by-site basis, orders of magnitude variations in mid-ocean ridge heat/helium fluxes are observed (Lupton *et al.* 1989, 1999; Turner & Stuart 1992). The numerical model investigating $^4\text{He}/\text{heat}$ variance illustrates that dynamically induced heterogeneity within a model of whole-mantle convection, combined with the requirement for the transport of He to mid-ocean ridges before its extraction, produces significant long-time-scale variance in surface $^4\text{He}/\text{heat}$ (van Keken *et al.* 2001). Superimposed over this long time-scale effect will be short-term temporal effects of the He extraction processes discussed above.

In the absence of a suitable tool to address the magnitude of these effects in detail, it is prudent to consider the consequence of indeed ‘living in special times’. The most obvious would be that volatile fluxes from the mantle must have been significantly higher than those observed today (on average by a factor of approximately four). Nevertheless, it is not straightforward to test this within the geological record. If the flux is higher, the mantle supplying mid-ocean ridges must in turn have a significantly higher ^3He concentration; within the models of whole-mantle convection this is approximately four times higher than that estimated from the ocean ^3He flux (figure 3).

6. The zero-paradox upper-mantle noble-gas concentration

The three most important noble-gas arguments for layering and mass transfer within the mantle system ($^3\text{He}/^4\text{He}$ difference between ocean-island and mid-ocean ridge volcanism; ^{40}Ar mass balance; and $^4\text{He}/\text{heat}$ imbalance) are founded on the calculated concentration of ^3He in the mantle supplying mid-ocean ridges. We have shown above that discarding the $^4\text{He}/\text{heat}$ constraint would require an upper mantle with a higher ^3He concentration. This would be a factor of approximately four times greater than the estimate from the ocean ^3He flux.

We can make the same calculation for the ^3He concentration in the upper mantle that would no longer require an external ^3He flux to balance the observed U + Th and $^3\text{He}/^4\text{He}$, and also the concentration of ^{40}Ar (and therefore ^3He) that would have to be in the upper mantle to account for the ‘missing’ Ar.

We first consider the average ^{40}Ar concentration in the whole mantle that would balance the mass of ^{40}Ar now in the atmosphere. The 240 ppm K in the BSE, with a mass of 4.032×10^{27} g, will have produced 1.94×10^{42} atoms ^{40}Ar over 4.5 Gyr. The ^{40}Ar derived from K decay now in the atmosphere is 0.992×10^{42} atoms ^{40}Ar (Ozima & Podosek 1983). Neglecting the *ca.* 3% ^{40}Ar trapped within the continental crust (Ballentine & Burnard 2002), this requires that 0.948×10^{42} atoms ^{40}Ar are within the mantle, which, if distributed homogeneously, would give a mantle ^{40}Ar

concentration of 2.36×10^{14} atoms ^{40}Ar per gram. This is a factor of 3.7 times greater than the estimate from the ocean ^3He flux.

Taking the concentration of U and Th in the mantle beneath mid-ocean ridges to be 0.008 ppm and 0.016 ppm, respectively (Jochum *et al.* 1983), and assuming closed-system evolution, some 3.12×10^{14} atoms ^4He per gram are produced over 4.5 Gyr. The measured $^3\text{He}/^4\text{He}$ ratio is $8Ra$ ($^3\text{He}/^4\text{He} = 1.12 \times 10^{-5}$). Assuming an initial $^3\text{He}/^4\text{He} = 120Ra$ (1.68×10^{-4}), this requires that the closed-system ^3He concentration is 3.75×10^9 atom ^3He per gram. This is a factor of 3.2 times greater than the estimate from the ocean ^3He flux.

It would appear that, if mid-ocean-ridge source noble-gas concentrations are around 3.5 times higher ($^3\text{He} = 4 \times 10^9$ atoms ^3He per gram) than current estimates, we would have a model in which there is:

- (1) no requirement for a mass flux from a high $^3\text{He}/^4\text{He}$ reservoir to buffer the upper-mantle ^3He concentration;
- (2) no large hidden ^{40}Ar -rich reservoir; and
- (3) ^4He /heat variation that is more readily ascribed to high temporal variability of ^4He loss.

We call this concentration the zero-paradox concentration and emphasize that this is a model reference value only. As the convecting mantle ^3He concentration approaches this value, the ^3He mass flux, hidden reservoir volume and strength of the ^4He /heat constraint on the requirement for a deep boundary layer, respectively, are reduced.

7. Evidence for higher noble-gas concentrations beneath mid-ocean ridges

The ^3He flux into the oceans has been regarded as a robust estimate because of its 1000 year time-integrated record. We have argued that 1000 years is still a very small time window within which to compare rates of ocean-crust generation. Other techniques for assessing the noble-gas concentration of the mantle (summarized in figure 4) must be considered. Direct determination of noble-gas concentrations in mid-ocean-ridge basalts is not straightforward, due to degassing of the magma on eruption followed by variable but non-fractionating secondary-gas loss (Moreira & Sarda 2000; Sarda & Moreira 2002), possibly due to vesicle rupture on collection or during laboratory disaggregation. One sample, the gas-rich IID43 ‘popping rock’ has received much attention. Pre-concentration of magmatic gas in the magma chamber appears to be ruled out on two counts: vesicle size distribution is consistent with continuous and simultaneous nucleation during magma ascent (Sarda & Graham 1990), and He/Ar, C/He and C/N ratio variations are consistent with closed-system formation during ascent (Javoy & Pineau 1991). Measured ^3He concentrations in this sample are *ca.* 2.69×10^{10} atoms ^3He per gram (Moreira *et al.* 1998; Sarda *et al.* 1988). At 10% partial melt, this sample then defines a *minimum* source concentration of 2.69×10^9 atoms ^3He per gram, which is 2.3 times higher than the ^3He flux estimate.

Another indication of higher mantle values is the estimate of carbon concentrations in MORBs based on graphite-melt equilibrium, giving an undegassed MORB

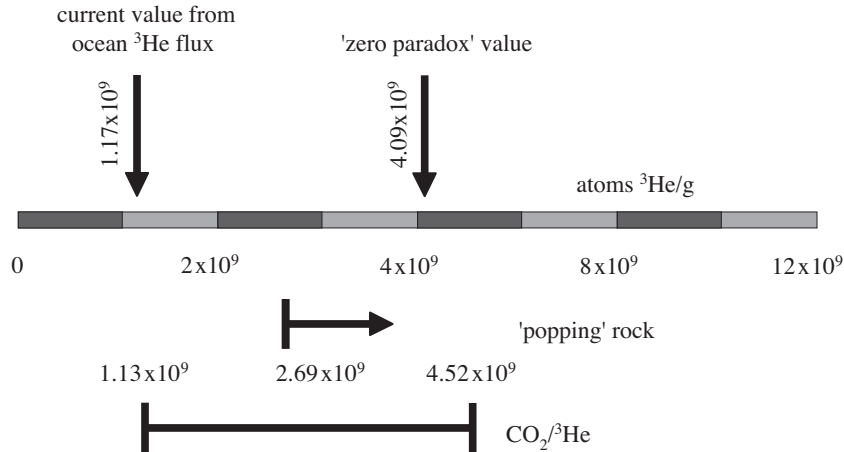


Figure 4. Comparison of different estimates of ^3He concentrations in the MORB mantle source assuming a 10% partial melt (see text). The zero-paradox value is the concentration at which there is no longer any requirement for ^3He addition to the upper mantle to buffer $^3\text{He}/^4\text{He}$ ratios and there is no hidden ^{40}Ar -rich reservoir. It is a value at which the $^4\text{He}/\text{heat}$ imbalance can be accounted for by short temporal variability in the ocean He flux.

carbon concentration of between 900 ppm and 1800 ppm (Holloway 1998). The relationship between magmatic $\text{CO}_2/{}^3\text{He}$ ratios is well established, with source values between 1×10^9 and 2×10^9 (Marty & Jambon 1987; Trull *et al.* 1993) to give undegassed-basalt ^3He concentrations in the range of 1.13×10^{10} – 4.52×10^{10} atoms ^3He per gram. At 10% partial melt this defines a source concentration of 1.13×10^9 – 4.52×10^9 atoms ^3He per gram, or between 1.0 and 3.9 times higher than the ^3He flux estimate.

Two independent estimates of noble-gas concentrations that approach or equal the zero-paradox value clearly show the weakness of noble-gas constraints on layering. A more accurate determination of noble-gas concentrations in the convecting mantle must remain a high priority to properly assess the constraints imposed on mantle models by these noble-gas tools.

8. Noble-gas concentrations in the ocean-island-basalt source

The steady-state noble-gas models make the implicit assumption that the lower mantle has remained a closed system for most of the Earth's history and that, as a closed system, it contains radioelement concentrations similar to that of the BSE. Taking BSE U and Th concentrations of 21 ppb and 75 ppb respectively (Jochum *et al.* 1983), 9.48×10^{14} atoms ^4He per gram are produced over 4.5 Gyr. With an initial $^3\text{He}/^4\text{He}$ ratio of $120Ra$, this requires the model ^3He concentration to be 9.6×10^{10} atoms ^3He per gram for a source with $^3\text{He}/^4\text{He} = 45Ra$ (6.55×10^{10} atoms ^3He for a source with $^3\text{He}/^4\text{He} = 35Ra$). This 'lower mantle' source-concentration prediction provides an important reference and test for the validity of the layered-mantle model and is comparable with the zero-paradox upper-mantle concentration of 4×10^9 atoms ^3He per gram.

Noble-gas concentration estimates of the ocean-island-volcanic mantle source are derived in the same way as the concentrations for the mid-ocean-ridge mantle source.

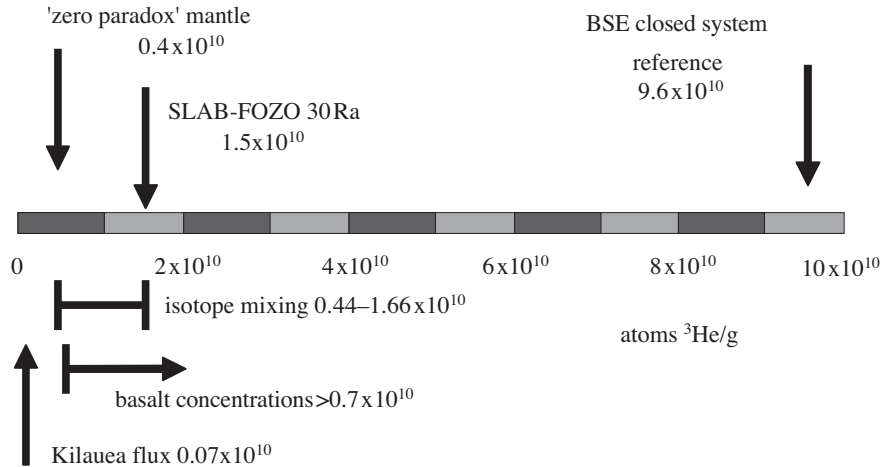


Figure 5. Two-component mixing. ^3He concentrations are shown for different estimates of oceanic-island mantle sources and are compared with model values (see text).

However, the flux of ^3He from the intraplate volcanic systems are dominantly sub-aerial and there is no available time-integrated degassing rate for ocean-island volcanics over even short geological periods. Estimates of the ^3He concentrations are limited to three approaches: combining estimates of magma generation rate, degree of partial melt and present-day ^3He flux estimate from individual sites; measurement of ^3He concentrations in basalt combined with a correction for gas loss during melting or upon eruption; and identification of isotopic mixing to resolve OIB end-member noble-gas concentrations. The various concentration estimates are shown in figure 5.

Measurement of, for example, the CO_2 flux from the summit and vents of Kilauea, Hawaii, combined with $\text{CO}_2/^3\text{He}$ and estimated magma production rate provides a local estimate of the undegassed magma of 1.3×10^{10} atoms ^3He per gram (Hilton *et al.* 1997). Taking a 5% partial melt, this gives a source ^3He concentration of 0.07×10^{10} atoms ^3He per gram, which is approximately 150 times lower than the closed-system model prediction. Temporal variation in CO_2 flux over the time-scale of the magma-generation rates remains unconstrained.

He concentration measured in Hawaiian basalts gives similarly low concentration estimates of the source, which, for a 5% partial-melt, range between 0.06×10^{10} and 0.19×10^{10} atoms ^3He per gram (Torgersen 1989). This is a minimum estimate, as there is no consideration of gas loss during eruption. Moreira & Sarda (2000) show that, for a filtered dataset, fractionated noble-gas abundance patterns in OIB glass reflect an open system-degassing process on eruption. Nevertheless, using the Rayleigh fractionation law, the magnitude of fractionation is consistent with only 10% He loss. Samples from the same source, with a similar degree of eruptive gas loss nevertheless show orders of magnitude difference in derived source concentration. Moreira & Sarda (2000) argue that this is due to secondary, and unfractionating, gas loss from these samples. In this context, the most gas-rich sample defines a minimum noble-gas concentration of 0.71×10^{10} atoms ^3He per gram, which is approximately 13 times lower than the closed-system model.

There are many examples of $^3\text{He}/^4\text{He}$ correlation with Sr, Nd or Pb isotopes in intraplate ocean-island volcanics (Kurz *et al.* 1982; Kurz & Kammer 1991; Farley

et al. 1993; Eiler *et al.* 1998; Kurz & Geist 1999). These correlations are assumed to be caused by mixing between the ocean-island and upper-mantle sources prior to eruption. Compilation of Sr–Nd–Pb–Hf–Os-isotope data is also consistent with two-component mixing at many of these intraplate volcanic sites. However, the component with similar $^3\text{He}/^4\text{He}$ ratios to mid-ocean ridges has an isotopic composition that for most intraplate systems cannot be simply related to the mid-ocean-ridge source mantle (Zindler & Hart 1986; Hauri *et al.* 1994; Hauri 1996). In this case, without a defined ‘upper-mantle’ end-member composition, it is not possible to resolve the character of the high $^3\text{He}/^4\text{He}$ source unambiguously. This is not the case at Iceland, where ocean-island volcanism occurs on a mid-ocean-ridge axis, and observed $^3\text{He}/^4\text{He}$ correlations with Pb can be used with more confidence to assess the character of the ocean-island mantle source.

Hilton *et al.* (2000) show linearly correlated $^3\text{He}/^4\text{He}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ on the Reykjanes ridge, Iceland. This is also the case for He concentrations in the limiting case where the Pb concentration of the Iceland source is the same as that of the mid-ocean-ridge source ([Pb] \approx 0.05 ppm). The $^3\text{He}/^4\text{He}$ of the Iceland end-member is four times higher than the mid-ocean-ridge source, giving an Icelandic mantle ^3He source concentration of between 0.44×10^{10} (taking the ^3He flux estimate) and 1.6×10^{10} (using the zero-paradox reference concentration) atoms ^3He per gram. This is a factor of between 21 and 6 below the closed-system-model value. Higher Icelandic source Pb concentrations increase this estimate, for example BSE Pb concentrations of 0.185 ppm increase the ^3He concentration range by a factor of 3.7 (Hilton *et al.* 2000).

9. Recycled material in the ocean-island-volcanic source and $^3\text{He}/^4\text{He}$

There is strong evidence that OIBs contain a significant proportion of material that has been recycled into the mantle, with a residence time of the order of *ca.* 1 Gyr (e.g. White & Hofmann 1982; Zindler & Hart 1986; Hauri *et al.* 1994; Hauri 1996; Eiler *et al.* 1996; Ballentine *et al.* 1997; Hofmann 1997; Sobolev *et al.* 2000). The incompatible and volatile nature of He means that recycled material will be almost quantitatively degassed and contains negligible ^3He . Subsequent ingrowth of ^4He by U and Th decay will result in a $^3\text{He}/^4\text{He}$ ratio far lower than that associated with ocean-island volcanism.

Investigation of $^3\text{He}/^4\text{He}$ correlation with radiogenic isotopes such as Sr, Nd and Pb shows that most ocean-island-volcanic systems display an elongated array consistent with two-component mixing (Zindler & Hart 1986; Hart *et al.* 1992; Hauri *et al.* 1994) (figure 6). This mixing represents heterogeneity within the mantle protolith rather than mixing with the upper-mantle system (Hauri *et al.* 1994; Ballentine *et al.* 1997). One of the protolith components has variable Sr-, Nd- and Pb-isotopic compositions and elevated $^{187}\text{Os}/^{188}\text{Os}$, which is characteristic of the recycled material, such as recycled oceanic crust (high μ (HIMU) mantle) with variable admixtures of sediments (EM1), ancient sediments or depleted lithosphere (EM2). This component is associated with lower $^3\text{He}/^4\text{He}$ ratios. The high $^3\text{He}/^4\text{He}$ component has a more distinct character (FOCUS ZONE (FOZO)), with the elongated arrays converging on a $^3\text{He}/^4\text{He} \approx 45Ra$ and $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.704$ (Hauri *et al.* 1994) (figure 6).

We present a simple calculation for mixing between FOZO and recycled oceanic crust (figure 7). We make the assumption that FOZO is slightly more depleted than

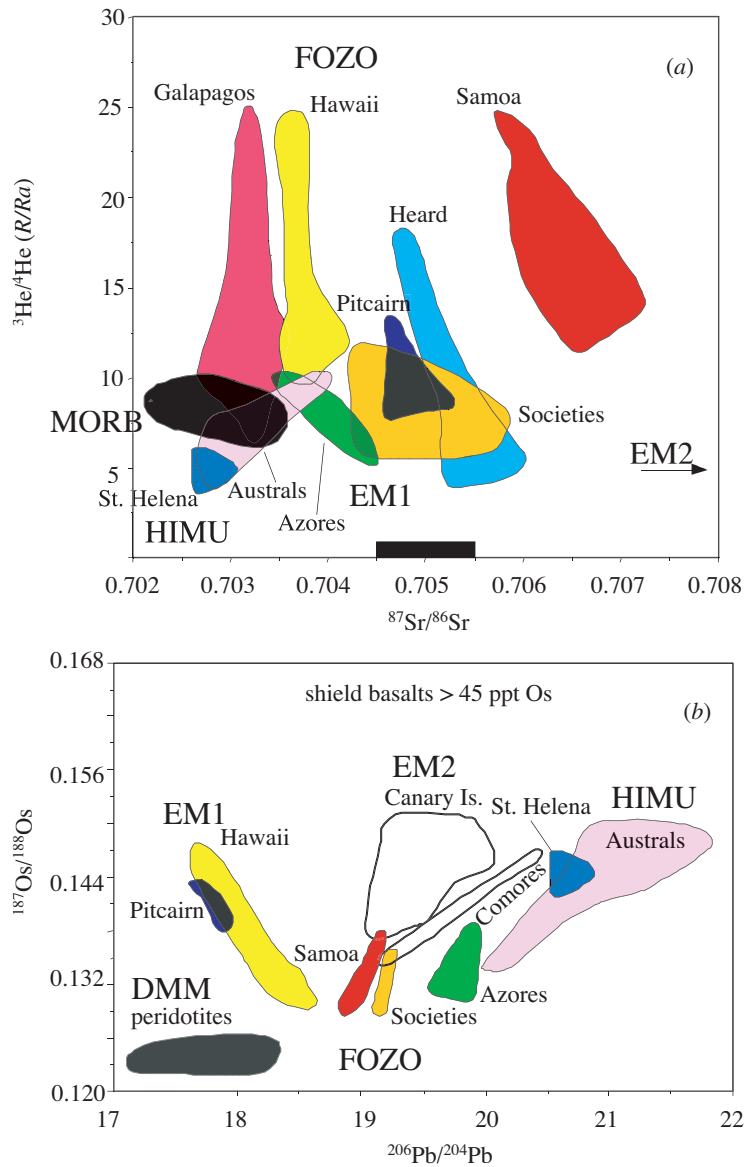


Figure 6. Mantle end-members from Zindler & Hart (1986) and Hauri *et al.* (1994). (Figure updated from Hauri *et al.* (1994) after van Keken *et al.* (2002).) (a) Sr–He and (b) Os–Pb-isotope correlations for oceanic basalts. All OIBs show elevated Os-isotope ratios, indicative of the presence of mafic material in EM1, EM2 and HIMU-type sources. Both data plots show elongated mixing arrays converging on the high- $^3\text{He}/^4\text{He}$ FOZO component. Data are averaged by island, volcano or geologic formation, except for Heard, Samoa and MORB, for which all data are plotted. Data and references can be found in the PETDB and GEOROC geochemical databases (<http://petdb.ldeo.columbia.edu/petdb/>; <http://georoc.mpch-mainz.gwdg.de/Start.asp>).

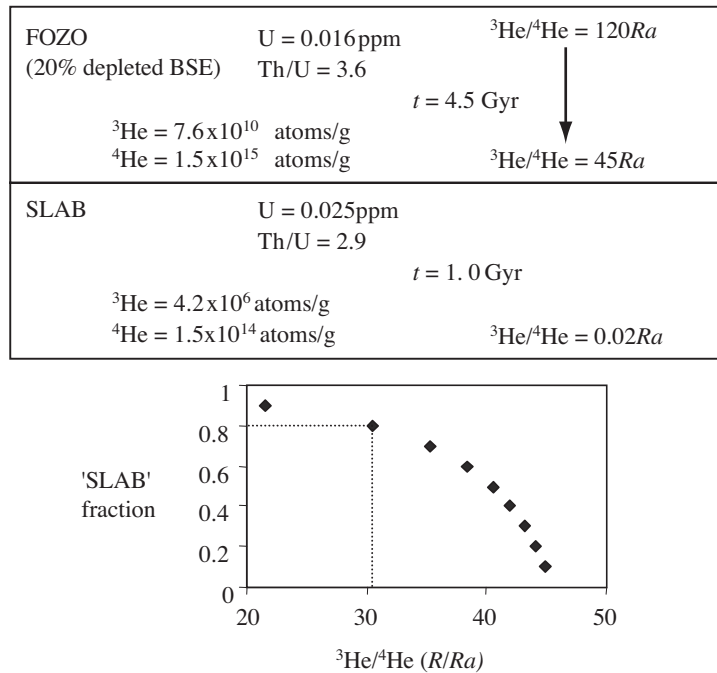


Figure 7. Two-component mixing, between recycled material that has been stored in the mantle for 1 Gyr and the FOZO component, assumed to be slightly depleted relative to BSE and to have evolved from ${}^3\text{He}/{}^4\text{He} = 120Ra$ to $45Ra$ over 4.5 Gyr. To generate a $30Ra$ mixture requires a 20% FOZO contribution to the slab, giving ${}^3\text{He} = 1.5 \times 10^{10}$ atoms ${}^3\text{He}$ per gram: a factor of 6.4 times lower than closed-system estimates and similar to values inferred using He- and Pb-isotope mixing (Hilton *et al.* 2000) (cf. figure 5). (A 2.5% FOZO admixture with the slab produces ${}^3\text{He}/{}^4\text{He} = 8Ra$, with 0.2×10^{10} atoms ${}^3\text{He}$ per gram.)

BSE values and that the He isotopes have evolved in this mantle component from $120Ra$ to $45Ra$ over 4.5 Gyr. This requires a ${}^3\text{He}$ concentration of 7.6×10^{10} atoms ${}^3\text{He}$ per gram, which is similar to the lower mantle in the layered-mantle models. Similarly, for the recycled oceanic crust, we assume that it is initially degassed and then stored in the mantle for 1 Gyr. To generate a mixture with ${}^3\text{He}/{}^4\text{He} = 30Ra$ we require a 20% FOZO contribution to the slab, giving a source ${}^3\text{He}$ concentration of the mix of 1.5×10^{10} atoms ${}^3\text{He}$ per gram. This is within the concentration range given by the Icelandic mixing study. It has previously been noted that the observed concentrations of ${}^3\text{He}$ in OIB samples are significantly lower than closed-system estimates would predict, and the discrepancy between model and observed values has been called the ‘helium paradox’ (Anderson 1998).

Within the context of the recycled material that dominates ocean-island volcanism, we should not expect to see the high ${}^3\text{He}$ concentrations predicted by the layered-mantle model. We find no paradox.

It has been observed that the mid-ocean-ridge mantle source may have a FOZO component (Hart *et al.* 1992; Farley *et al.* 1992; Hanan & Graham 1996). A similar calculation can be done for the mantle supplying mid-ocean ridges, assuming that this was depleted and degassed, has remained a closed system for 4.5 Gyr and has mixed with a small portion of FOZO. Taking the concentrations of U and Th in the mantle

beneath mid-ocean ridges to be 0.008 ppm and 0.016 ppm, respectively (Jochum *et al.* 1983), and assuming closed-system evolution, some 3.12×10^{14} atoms ^4He per gram are produced over 4.5 Gyr. To produce the observed $8Ra$, a 5.3% FOZO contribution is required, which gives the upper-mantle zero-paradox ^3He concentration of 4×10^9 atoms ^3He per gram.

10. Conclusions

With the development of geochemical tracing within numerical models of mantle convection, processes often confined to cartoons or prescribed processes within box models can be investigated quantitatively within the constraints imposed by the fluid dynamics, rheology, phase changes and heat flow of the Earth. Combined with advances in high-resolution seismic tomography, these studies produce results that are not consistent with geochemical models advocating layering of the mantle at the 670 km discontinuity. We have reviewed the evolution of the geochemical layered-mantle model and, in particular, the layered models developed to account for observed variations in noble-gas isotopic compositions, flux and mass balance. We have shown that the requirement for a ^3He flux into the upper mantle, an ^{40}Ar -rich lower mantle and a model in which a deep boundary layer separates ^4He from heat are inexorably linked to the ^3He concentration of the upper mantle that has been derived from the present-day ^3He flux into the oceans. If the concentration of the mantle supplying mid-ocean ridges (the convecting mantle) is a factor of 3.5 times higher than the ocean-flux model, then the following apply.

- (1) The upper-mantle $^3\text{He}/^4\text{He}$ does not require an input from a higher $^3\text{He}/^4\text{He}$ source.
- (2) The ^{40}Ar in a uniform-concentration whole mantle, together with the mass of ^{40}Ar in the atmosphere, balances the mass of ^{40}Ar produced by K decay over the Earth's history.
- (3) The imbalance between heat and helium can be explained by short-time-scale variance of the mantle ^3He flux into the oceans in combination with large-scale dynamic variance.

This high noble-gas concentration in the convecting mantle is a model value that we call the zero-paradox concentration.

We show that gas-rich basalts and carbon concentrations in the MORBs provide evidence for an upper mantle with a ^3He concentration possibly twice as high as ^3He ocean-flux estimates. As the zero-paradox concentration is approached, the mass of the mantle required to preserve high ^{40}Ar concentrations is strongly reduced and the geochemical argument for convective mantle layering is removed. This then allows for small-scale geochemical heterogeneity to account for the observed noble-gas isotopic $^3\text{He}/^4\text{He}$ variation and $^4\text{He}/\text{heat}$ imbalance. We also show that, by considering OIBs to be dominantly recycled ocean crust, a small admixture of a mantle component (FOZO) that has both high $^3\text{He}/^4\text{He}$ and high helium concentrations can account for both the observed ocean-island $^3\text{He}/^4\text{He}$ and ^3He concentrations. The formation and processes that have resulted in the preservation of the FOZO component within the mantle will remain a key geochemical constraint in the development of the dynamic-mantle model, together with the open question regarding the nature of the process

that results in the mixing of recycled material, and possibly the mid-ocean-ridge source mantle, with FOZO. We find no paradoxes in the noble-gas systematics of the mantle.

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