

# On the origin of noble gases in mantle plumes

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The chemical differences between deep- and shallow-mantle sources of oceanic basalts provide evidence that several distinct components coexist within the Earth's mantle. Most of these components have been identified as recycled in origin. However, the noble-gas signature is still a matter of debate and questions the preservation of primitive regions in the convective mantle. We show that a model where the noble-gas signature observed in Hawaii and Iceland comes from a pristine homogeneous deep layer would imply a primitive <sup>3</sup>He content and <sup>3</sup>He/<sup>22</sup>Ne ratio that are very unlikely. On the contrary, mass balances show that the partly degassed peridotite of a marble-cake mantle can be the noble-gas end-member with an apparent 'primitive'-like composition. This component is mixed with recycled oceanic crust in different proportions in the plume sources and in the shallow mantle. A recycling model of the mantle, involving gravitational segregation of the oceanic crust at the bottom of the mantle, potentially satisfies trace-element as well as noble-gas constraints.

**Keywords:** mantle; noble gas; plumes; recycling; convection

## 1. Introduction

Isotope geochemistry of mantle-derived rocks provides fundamental information about the mantle's chemical structure and dynamics. Systematic chemical differences between mid-ocean ridge basalts (MORBs) and oceanic basalts (OIBs) are observed and show that chemically different domains coexist within the Earth's mantle (Zindler & Hart 1986; Hofmann 1997). Global mass balances have shown that significant portions of the mantle have to be richer in trace elements than in the shallow mantle (Jacobsen & Wasserburg 1979; Davies 1981). Although the nature of these regions cannot be determined from this approach, further insights are expected from isotopic studies of mantle-derived basalts.

The identification of the isotopic end-members is a direct interpretation of the isotopic ratios measured in oceanic basalts. Isotopic systems like <sup>18</sup>O–<sup>16</sup>O, U–Pb, Lu–Hf and Re–Os have been used as fingerprints to identify recycled crustal components in the sources of Polynesia (Hauri & Hart 1993), Hawaii (Eiler *et al.* 1996; Blichert-Toft *et al.* 1999a) and Iceland (Chauvel & Hémond 2000) among others. The difficulties in understanding the isotopic signal of oceanic basalts come mostly from

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noble gases. Some hotspots, like Loihi and Iceland, have significantly lower  $^4\text{He}/^3\text{He}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios than MORBs (Kurz *et al.* 1982; Sarda *et al.* 1988; Dixon *et al.* 2000). Since  $^3\text{He}$  and  $^{22}\text{Ne}$  are primordial isotopes, contrary to the radiogenic  $^4\text{He}$  and nucleogenic  $^{21}\text{Ne}$ , it is commonly assumed that Loihi and Iceland are derived from pristine, undegassed portions of the mantle. In addition, the  $^{40}\text{Ar}$ – $^{40}\text{K}$  budget of the mantle tends to favour the existence of an undegassed reservoir in the lower mantle (Allègre *et al.* 1996).

The understanding of the geochemical signal is closely related to the competition between recycling degassed products and preserving undegassed regions in vigorous convection. The most recent geophysical observations show clear evidence of deep subduction. Global tomography over North America indicates that the Farallon plate is sinking through the whole mantle (Grand 1987; van der Hilst *et al.* 1997). This mode of convection is also able to explain more than 80% of geoid anomalies (Ricard *et al.* 1993). In a range of Earth-like parameters, convection calculations predict a deep-mantle flow and reproduce many of the observables (Bunge *et al.* 1998). In this context, the preservation of large-scale primitive regions is very unlikely, as is suggested by several mixing studies (van Keken & Ballentine 1998; Ferrachat & Ricard 2001).

Strictly speaking, mantle convection implies stirring, i.e. stretching and folding, not mixing, since chemical diffusion is negligible. The survival of highly deformed primitive veins in the mantle is likely. Even in the case of random distribution of subducted material in the mantle, the proportion of mantle rocks that have never been processed at ridges would never be zero but would decrease exponentially with a residence time  $F/M$  comparable with the age of the Earth (where  $M$  is the mantle mass and  $F$  the mass flux of subducted material). Stirring is certainly more complex than simple random redistribution, but all numerical simulations agree that a small but significant volume of material (from 10 to 35%) has not seen the surface (van Keken & Ballentine 1998; Ferrachat & Ricard 2001; Coltice *et al.* 2000*b*).

Keeping any sort of chemical layering implies the existence of a stabilizing density stratification, and preserving an undegassed abyssal layer in the deep mantle requires that primitive rocks are slightly denser than the overlying differentiated material (Kellogg *et al.* 1999). Another point of view is that chemical layering is an ongoing process as a consequence of plate tectonics: the dense eclogitic oceanic crust can accumulate at the bottom of the mantle by gravitational segregation (Christensen & Hofmann 1994). This model could also explain various geochemical observations (Coltice & Ricard 1999; Ferrachat & Ricard 2001). In this paper, we attempt to identify the origin of the ‘primitive’-like noble-gas signature observed in several hotspots, in order to evaluate various mantle models.

## 2. Noble-gas constraints on mantle heterogeneity

### (a) Isotopic ratios

Noble-gas systematics of oceanic basalts show significant differences between the shallow-mantle source of MORBs and the sources of several OIBs, particularly Loihi (Kurz *et al.* 1982; Valbracht *et al.* 1997; Tieloff *et al.* 2000) and Iceland (Dixon *et al.* 2000; Tieloff *et al.* 2000; Harrison *et al.* 1999). These differences are identified by the ratios of radiogenic or nucleogenic isotopes over primordial isotopes, mostly  $^4\text{He}/^3\text{He}$ ,  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$ .  $^4\text{He}$  and  $^{21}\text{Ne}$  are produced through the radioactive decay

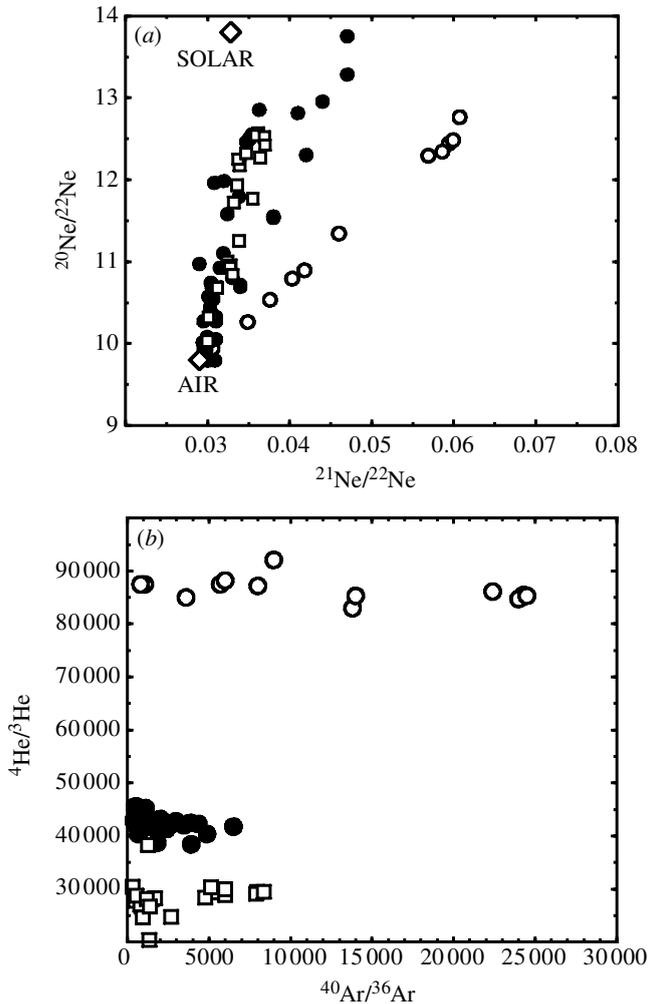


Figure 1. Neon isotope plot and argon–helium isotope plot for the popping rock (open circles (Moreira *et al.* 1998)), Iceland samples (filled circles (Dixon *et al.* 2000; Trieloff *et al.* 2000; Harrison *et al.* 1999)) and Loihi samples (open squares (Valbracht *et al.* 1997; Trieloff *et al.* 2000)).

of  $^{235,238}\text{U}$  and  $^{232}\text{Th}$ , whereas  $^{40}\text{Ar}$  is produced from  $^{40}\text{K}$  by electron capture. A fundamental problem in noble-gas geochemistry is that the initial isotopic signature of a basalt is often perturbed by the addition of atmospheric gases (except for helium, which is lost into space out of the atmosphere) (Ballentine & Barford 2000). Correcting for air contamination can be performed using the ratio of two stable isotopes of neon,  $^{20}\text{Ne}/^{22}\text{Ne}$  (Farley & Poreda 1993), which is presumed to be solar or maybe meteoritic (Trieloff *et al.* 2000).

When corrected from atmospheric contamination, MORBs show systematically higher radiogenic/primordial ratios compared with Loihi and Iceland, as depicted in figure 1. These differences are attributed to lower  $^3\text{He}/(\text{Th}+\text{U})$ ,  $^{22}\text{Ne}/(\text{Th}+\text{U})$  and  $^{36}\text{Ar}/\text{K}$  in the shallow mantle. The standard model argues for a primitive component

Table 1. *Typical isotopic composition of the shallow mantle and 'primitive'-like plumes* (Shallow-mantle data from Moreira *et al.* (1998), Loihi data from Trieloff *et al.* (2000) and Valbracht *et al.* (1997) and Iceland data from Dixon *et al.* (2000), Trieloff *et al.* (2000) and Harrison *et al.* (1999).)

	$^4\text{He}/^3\text{He}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{21}\text{Ne}/^{22}\text{Ne}$
shallow mantle	80 000–90 000	30 000–45 000	>0.07
Loihi	24 000–40 000	2 500–8 500	0.03–0.04
Iceland	20 000–40 000	3 000–8 000	0.03–0.04

in the source of plumes, rich in primordial noble gases (Porcelli & Wasserburg 1995). That assumption will be discussed below. Whatever the model, at least two components have to coexist within the mantle and they must have significant differences in ratios between primordial rare gases and radiogenic parent.

(b) *Helium concentrations*

The  $^4\text{He}$  abundance in the shallow mantle can be deduced from the  $^4\text{He}$  degassing flux from the mantle (Jean-Baptiste 1992; Farley *et al.* 1995). This flux is measured with a large uncertainty, *ca.*  $9 \times 10^7$  mol yr $^{-1}$ . The emplacement rate of oceanic crust is close to  $6 \times 10^{16}$  g yr $^{-1}$ . Consequently, the  $^4\text{He}$  content of the undegassed magma should be  $1500 \times 10^{-12}$  mol g $^{-1}$ . Assuming that helium is incompatible and that the newly formed oceanic crust comes from *ca.* 10% partial melting gives a  $^4\text{He}$  content of *ca.*  $150 \times 10^{-12}$  mol g $^{-1}$ . The uncertainty on this value is at least a factor of two, but we consider for numerical applications that the upper bound is *ca.*  $300 \times 10^{-12}$  mol g $^{-1}$ . A larger value would not invalidate our conclusions.

The  $^4\text{He}$  content in the source of Loihi cannot be computed directly; however, it has been noted that OIBs have low helium concentrations with respect to MORBs. This observation is referred to as the 'helium paradox', since OIBs are thought to derive from less-degassed sources (Anderson 1998). Can some kind of helium loss rule out this paradox? One way to estimate the helium loss is to compare the  $^3\text{He}/\text{U}$  ratio of OIBs and MORBs (the He/U ratio in the magma is identical to that in the source, as they are both very incompatible). According to their low  $^4\text{He}/^3\text{He}$  ratio, OIBs should have higher  $^3\text{He}/\text{U}$  ratios than MORBs. A typical uranium-content measurement in Loihi is three to four times higher than that in a fresh MORB (Sims & De Paolo 1997), so the helium content of a Loihi magma prior to degassing has to be, at least, three to four times that of MORBs. This indicates that most of the original helium is degassed before the magma reaches the surface. Hence, part of the 'helium paradox' is due to near-surface degassing.

(c)  $^3\text{He}/^{22}\text{Ne}$

Another constraint comes from the measured elemental composition. One must keep in mind that the elemental composition of samples can be fractionated by partial melting and degassing processes (Moreira & Sarda 2000). However, it is possible to estimate  $^3\text{He}/^{22}\text{Ne}$  in the different mantle sources using the production ratio  $^{21}\text{Ne}/^4\text{He}$  of  $4.5 \times 10^{-8}$  (Yatsevich & Honda 1997) (both  $^{21}\text{Ne}$  and  $^4\text{He}$  are produced

by the decay of U and Th),

$$\frac{{}^3\text{He}}{{}^{22}\text{Ne}} = \frac{{}^3\text{He}}{{}^4\text{He}} \frac{{}^{21}\text{Ne}}{{}^{22}\text{Ne}} \frac{{}^4\text{He}}{{}^{21}\text{Ne}}, \quad (2.1)$$

where  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$  is corrected for air contamination. Using the values of table 1,  ${}^3\text{He}/{}^{22}\text{Ne}$  is around 13 for MORBs and for both Loihi and Iceland samples (Harrison *et al.* 1999). However the  ${}^3\text{He}/{}^{22}\text{Ne}$  measured directly on a popping rock (i.e. a highly vesiculated basalt) (Moreira *et al.* 1998) and on Loihi glasses (Valbracht *et al.* 1997) is around seven. But whatever the preferred values, the different studies lead to the same idea: both ‘primitive’-like OIB and MORB sources have roughly similar  ${}^3\text{He}/{}^{22}\text{Ne}$  (Honda & Patterson 1999). The elemental ratio  ${}^3\text{He}/{}^{36}\text{Ar}$  is significantly more difficult to retrieve because of the difficulties in correcting for atmospheric  ${}^{36}\text{Ar}$  and because the production ratio  ${}^4\text{He}/{}^{40}\text{Ar}$  is a function of the age of the closed system (unlike  ${}^{21}\text{Ne}$  and  ${}^4\text{He}$ ,  ${}^{40}\text{Ar}$  and  ${}^4\text{He}$  do not belong to the same decay chain).

The relative constancy of  ${}^3\text{He}/{}^{22}\text{Ne}$  among oceanic basalts is surprising, as He and Ne are fractionated in the residue after partial melting. This observation means either that the shallow and deep mantles have undergone the same degassing history or that a similar gas-rich component is present in both regions.

### 3. A primitive layer as the origin of plume noble gases?

A primitive homogeneous layer supplying noble gases in mantle plumes is a frequent hypothesis. However, this section shows some of the limitations and inherent contradictions of this model.

#### (a) Primitive fraction in mantle plumes

In the model involving the persistence of pristine regions in the mantle, the ‘primitive’-like noble-gas signature of some OIBs (‘oib’) derives from a mixing between the shallow mantle (SM) and a mass fraction  $f$  of a primitive mantle (PM) source (see figure 2). For simplicity we neglect the recycling components that are also present in OIBs.

For example, the mass-balance equations for any isotope concentration  $[X]$  reads:

$$[X]_{\text{oib}} = f[X]_{\text{PM}} + (1 - f)[X]_{\text{SM}}. \quad (3.1)$$

In this equation,  $X$  can be substituted by either  $R$  (a radiogenic isotope like  ${}^{40}\text{Ar}$  or  ${}^4\text{He}$ ) or  $P$  (a primitive isotope like  ${}^{36}\text{Ar}$  or  ${}^3\text{He}$ ). With a little algebra, we get

$$[R]_{\text{SM}} = [R]_{\text{PM}} \frac{f}{1 - f} \frac{(P/R)_{\text{PM}} - (P/R)_{\text{oib}}}{(P/R)_{\text{oib}} - (P/R)_{\text{SM}}}. \quad (3.2)$$

Applying the previous equation to the  ${}^{40}\text{Ar}$ – ${}^{36}\text{Ar}$  system can provide a fair estimate of  $f$  because the mantle–atmosphere system is closed for argon, and all the terrestrial  ${}^{40}\text{Ar}$  comes from the decay of  ${}^{40}\text{K}$ . The primitive  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  of the mantle cannot exceed 400, assuming that the shallow mantle, atmosphere and continental crust are complementary ( $(P/R)_{\text{PM}} \sim 1/400$ ) (Turner 1989). The  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  of OIB and SM are chosen from the measured values of 2500 (lower bound for Loihi,  $(P/R)_{\text{oib}} \sim 1/2500$ ) and 40 000 ( $(P/R)_{\text{SM}} \sim 1/40\,000$ ), respectively (see table 1).

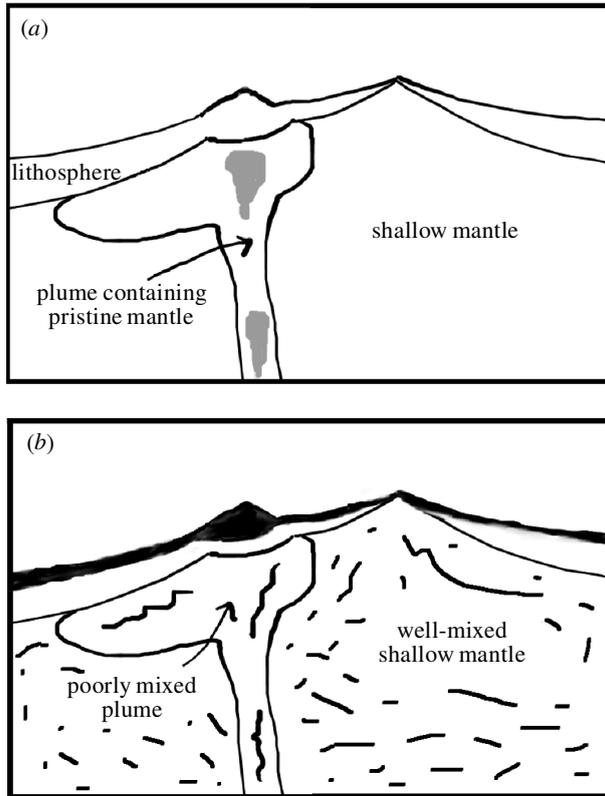


Figure 2. Schematic sketches of alternative models for 'primitive'-like plume noble gases. (a) Noble gases of OIBs are explained by the presence of pristine material in plumes. (b) Variable mixings of oceanic crust and residual peridotite provide the noble-gas variety of oceanic basalts.

A present-day  $[^{40}\text{Ar}]_{\text{PM}}$  of  $ca. 940 \times 10^{-12} \text{ mol g}^{-1}$  can be estimated from a primitive potassium content of 240 ppm (McDonough & Sun 1995).  $[^{40}\text{Ar}]_{\text{SM}}$  is difficult to measure accurately. However, a range of acceptable values for the  $^{40}\text{Ar}$  concentrations can be determined from the  $^4\text{He}/^{40}\text{Ar}$  measured in a popping rock to be 1.5 provides an upper bound for the shallow mantle  $^{40}\text{Ar}$  content of  $200 \times 10^{-12} \text{ mol g}^{-1}$  (Moreira *et al.* 1998). This value implies a  $^{40}\text{Ar}$  degassing flux of  $1.2 \times 10^7 \text{ mol yr}^{-1}$  in agreement with observations (Stuart & Grenville 1998).

All these concentration and ratio estimates used in equation (3.2) lead to an upper bound value of  $f$  of only 3% in the source of Loihi basalts. The conclusion is therefore

$$[^{40}\text{Ar}]_{\text{oib}} \sim [^{40}\text{Ar}]_{\text{SM}}, \quad (3.3)$$

$$[^{36}\text{Ar}]_{\text{oib}} \sim f[^{36}\text{Ar}]_{\text{PM}}. \quad (3.4)$$

The primitive mantle is so rich in primitive  $[^{36}\text{Ar}]$  that even a minute fraction of it suffices to give Loihi its primitive flavour. This is not the case for the radiogenic  $[^{40}\text{Ar}]$ , which is not affected by a few per cent of primitive material. This is not the case for common trace elements either. For example, 3% of primitive mantle having a uranium content of 21 ppb, will only contribute to 5% of the uranium content of the plume source, assuming 8 ppb of uranium in the shallow mantle (Zindler & Hart

1986). In the hypothesis of a primitive layer supplying noble gases, the composition and isotope ratios of incompatible refractory elements in the sources of Loihi or Iceland should be similar to those of the source of MORBs.

(b) *Elemental composition of the primitive material*

Now that we know that the fraction of primitive material in plumes is small ( $f \sim 3\%$ ), we can estimate the  $^3\text{He}$  content in the primitive material. Reformulating equation (3.2), we get

$$[P]_{\text{PM}} = [R]_{\text{PM}} \left( \frac{P}{R} \right)_{\text{oib}} + \frac{1-f}{f} [R]_{\text{SM}} \left\{ \left( \frac{P}{R} \right)_{\text{oib}} - \left( \frac{P}{R} \right)_{\text{SM}} \right\}, \quad (3.5)$$

where we use  $P = ^3\text{He}$  and  $R = ^4\text{He}$ .

A source of uncertainty in the numerical estimate comes from  $[^4\text{He}]_{\text{PM}}$  because an unconstrained quantity of  $^4\text{He}$  must have been trapped during Earth's accretion. But the closed-system production ratio  $^4\text{He}/^{40}\text{Ar}$  of 1.5 gives a lower bound for  $[^4\text{He}]_{\text{PM}}$ . The other quantities have already been discussed. The obtained primitive  $^3\text{He}$  is then a lower bound, *ca.*  $0.2 \times 10^{-12} \text{ mol g}^{-1}$ , slightly higher than the value computed by Harper & Jacobsen (1996) from a comparable analysis. This value is as high as the concentration of typical carbonaceous chondrites (Mazor *et al.* 1970). However, shock experiments suggest that more than 99% of the initial volatile content of the parent bodies should have been degassed during Earth's accretion (Tyburczy *et al.* 1986). For that reason, it has been proposed that such a high helium content has been trapped from a solar composition proto-atmosphere (Harper & Jacobsen 1996) or from an He-rich reservoir such as interplanetary dust particles (Pepin *et al.* 2001). In any case, the primitive mantle should have been very rich in rare gases and the extensive degassing of the upper mantle (99%) should not have fractionated the residual helium and neon.

#### 4. A degassed and ubiquitous source for 'primitive'-like noble gases

(a) *Noble gases in the marble-cake mantle*

As the hypothesis of a primitive deep mantle seems to lead to various contradictions, the 'pristine'-like noble-gas isotopic ratios are probably derived from a source that has experienced some degree of degassing. There are two ubiquitous components in the mantle: partly degassed peridotite and stirred ancient oceanic crust (the partly degassed peridotite being itself a mixture of stirred lithospheric mantle and of primordial mantle). These components have been identified petrologically and geochemically in peridotite massifs and MORBs (Pearson *et al.* 1991; Blichert-Toft *et al.* 1999b; Eiler *et al.* 2000). The convective mantle, made from pyroxenite layers embedded in a matrix of peridotite, looks like a marble cake (Allègre & Turcotte 1986).

In the marble-cake mantle, the radiogenic noble gases are concentrated in the stirred oceanic crust, rich in uranium, thorium and potassium. The crust has lost most of its primordial volatiles and, consequently, the peridotite should be the reservoir of primordial noble gases. These two components therefore have different noble-gas signatures and mixing them in variable proportions could explain the heterogene-



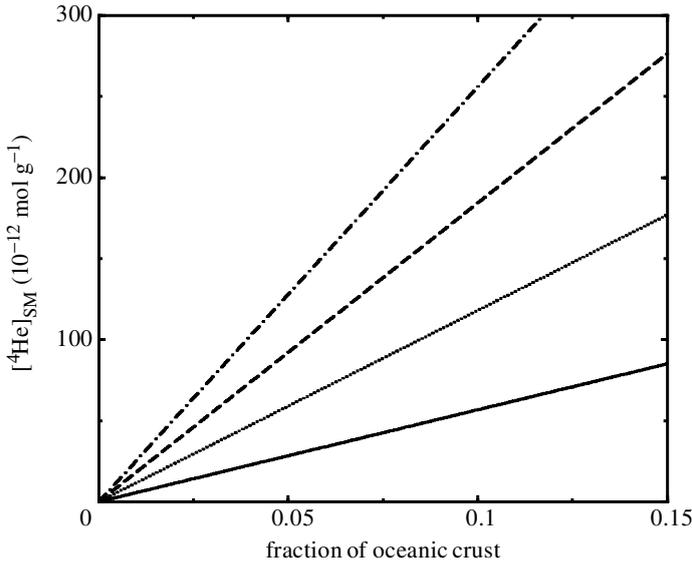


Figure 4.  ${}^4\text{He}$  concentration in the shallow mantle modelled as a function of the fraction of recycled oceanic crust in a marble-cake mantle. Different accumulation times of  ${}^4\text{He}$  in the oceanic crust are represented: —, 500 Myr;  $\cdots\cdots\cdots$ , 1000 Myr; ---, 1500 Myr;  $-\cdot-\cdot-\cdot-$ , 2000 Myr. The observed shallow mantle  ${}^4\text{He}$  content ranges from 100 to  $300 \times 10^{-12} \text{ mol g}^{-1}$ .

in the shallow mantle:

$$[{}^4\text{He}]_{\text{SM}} = (1 - f_c)[{}^4\text{He}]_{\text{per}} + f_c[{}^4\text{He}]_{\text{crust}}, \quad (4.1)$$

$$\left(\frac{{}^3\text{He}}{{}^4\text{He}}\right)_{\text{SM}} = (1 - f_c)\frac{[{}^4\text{He}]_{\text{per}}}{[{}^4\text{He}]_{\text{SM}}}\left(\frac{{}^3\text{He}}{{}^4\text{He}}\right)_{\text{per}} + f_c\frac{[{}^4\text{He}]_{\text{crust}}}{[{}^4\text{He}]_{\text{SM}}}\left(\frac{{}^3\text{He}}{{}^4\text{He}}\right)_{\text{crust}}. \quad (4.2)$$

The concentration of radiogenic nuclides in the recycled oceanic crust is a function of its radioactive-element content (70 ppb of uranium for typical fresh MORBs (Hofmann 1988)) and its age. The  ${}^4\text{He}/{}^3\text{He}$  in the ancient oceanic crust should be very high (*ca.*  $10^7$ ) compared with MORBs, since it has lost most of its primordial rare gases by shallow degassing. Therefore, the peridotite has to appear more primordial than the MORB source. For simplicity, the peridotite is assumed to be the ‘primitive’-like isotopic end-member in OIBs in this model (i.e.  $({}^4\text{He}/{}^3\text{He})_{\text{per}} = ({}^4\text{He}/{}^3\text{He})_{\text{oib}} = 20\,000$ ). Three unknowns are dominant in this problem:  $f_c$ , the fraction of recycled crust in the shallow mantle, the age of this crust and the  ${}^4\text{He}$  content of the shallow mantle. The relationships between these variables are shown in figure 4.

For the previously estimated range of shallow mantle  ${}^4\text{He}$  abundance, the modelled age of the crust is likely to lie between 1 and 2 billion years, corresponding to a value of  $f_c$  greater than 3%. This amount of recycled crust would provide at least 2 ppb of uranium in the MORB source, so that the peridotite would have a concentration of uranium of a few parts per billion.

How do these predictions compare with first-order observations? The  ${}^4\text{He}/\text{U}$  ratio of mantle melts can be used to determine an approximate accumulation time of  ${}^4\text{He}$  of the shallow-mantle source, especially because both uranium and helium are supposed to be very incompatible elements and should not be fractionated in the melts. The

previous estimates for the flux of  $^4\text{He}$  and U content in the oceanic crust lead to an accumulation time of more than 1.7 billion years for the mid-ocean-ridge source rocks, with an uncertainty of 50%. The same result can be reached by calculating the  $^4\text{He}$  accumulation time for the popping rock ( $[^4\text{He}] \sim 390 \times 10^{-12} \text{ mol g}^{-1}$ ), assuming a uranium content comparable with 70 ppb, typical of fresh MORBs. The fraction of crust within the shallow mantle is difficult to estimate, but most of the geological studies of peridotitic massifs and MORB chemistry provide estimates ranging from 2 to 10% (Pearson *et al.* 1991; Blichert-Toft *et al.* 1999b; Eiler *et al.* 2000; Allègre & Turcotte 1986). The observations concerning the ‘age’ and the fraction of recycled crust of the shallow mantle confirm that, to first order, a partly degassed peridotite can account for ‘primitive’-like noble-gas ratios.

The non-radiogenic noble gases in the shallow mantle mostly reside in the peridotite. The recycled crust is strongly degassed and hence equation (4.2) is well approximated by

$$[^3\text{He}]_{\text{SM}} \sim (1 - f_c)[^3\text{He}]_{\text{per}}, \quad (4.3)$$

and this is certainly true for most of the stable rare-gas isotopes. Hence, the model predicts that the amounts of  $^3\text{He}$ ,  $^{22}\text{Ne}$  and  $^{36}\text{Ar}$  are the same in the shallow mantle and the ‘primitive’-like plume source. We consider that this prediction is consistent with observation (Honda & Patterson 1999; Moreira *et al.* 2001).

The present-day  $^3\text{He}$  content of the shallow mantle, deduced from degassing observations, is close to  $1.5 \times 10^{-15} \text{ mol g}^{-1}$  and hence approximately 100 times smaller than the chondritic value. Several numerical simulations show that convection dynamics, incorporating melting, degasses no more than *ca.* 65% of the primordial  $^3\text{He}$  (van Keken & Ballentine 1998; Ferrachat & Ricard 2001). Hence, the prediction of the  $^3\text{He}$  content by the marble-cake mantle model is consistent with whole-mantle thermochemical calculations, using a 98.5% degassed chondrite as a proxy for the primitive Earth, i.e. it does not require to start from a gas-rich mantle.

The proposed origin of ‘primitive’-like noble gases seems to be consistent with the present-day rare-gas data of MORBs and OIBs. The most-simplified version of the model has been described here. The difference in age between OIB and MORB sources, and the impact of possible atmospheric volatile recycling (Sarda *et al.* 1999) could potentially change some details.

## 5. The argon constraint: a deep reservoir of radiogenic gases

If the isotopic heterogeneity is the most controversial aspect of the geochemistry of mantle noble gases, the global budget of  $^{40}\text{Ar}$  is certainly a crucial issue as well. The  $^{40}\text{Ar}$  economy of the Earth potentially gives information on the degree of degassing of mantle reservoirs. Previous studies argue that the atmosphere and the upper mantle only combine for 60% of the global budget of  $^{40}\text{Ar}$ , leaving the remaining 40% to an undegassed reservoir in the deep mantle (Allègre *et al.* 1996). Some knowledge of the potassium content in the primordial mantle is required to reach this conclusion. The proposed potassium concentration is determined by scaling to the better-established uranium concentration, assuming that potassium and uranium never fractionate among physical and chemical processes (Jochum *et al.* 1983). Albarède (1998) pointed out that this assumption could be falsified and a lower primitive K/U would question the robustness of the  $^{40}\text{Ar}$  budget constraint on

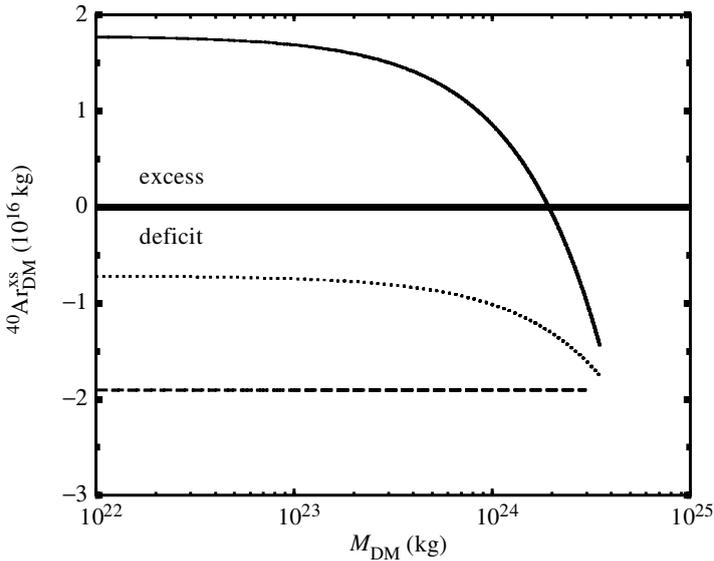


Figure 5.  $^{40}\text{Ar}$  excess of a deep-mantle reservoir predicted, taking into account the uncertainties in potassium and argon concentrations in the shallow mantle: —, shallow-mantle concentrations of 80 ppm of potassium and  $50 \times 10^{-12} \text{ mol g}^{-1}$  of  $^{40}\text{Ar}$ ; ···, shallow-mantle concentrations of 50 ppm and  $100 \times 10^{-12} \text{ mol g}^{-1}$ ; - - -, the hypothesis of closed-system shallow mantle.

mantle structure. His arguments are well illustrated by the variability of K/U among oceanic basalts (Halliday *et al.* 1995).

The  $^{40}\text{Ar}$  budget of the silicate Earth is given by

$$(^{40}\text{K}_{\text{CC}} + ^{40}\text{K}_{\text{SM}} + ^{40}\text{K}_{\text{DM}})R(e^{\lambda T} - 1) = ^{40}\text{Ar}_{\text{Atm+CC}} + ^{40}\text{Ar}_{\text{SM}} + ^{40}\text{Ar}_{\text{DM}}, \quad (5.1)$$

where  $^{40}\text{K}$  and  $^{40}\text{Ar}$  denote the masses of potassium-40 and argon-40. The different reservoirs considered are the atmosphere (Atm), the continental crust (CC), the shallow mantle (SM) and the deep mantle (DM).  $R$  is the branching ratio,  $\lambda$  is the radioactive decay constant of potassium-40 and  $T$  is the age of the Earth. However, the  $^{40}\text{Ar}$  budget can be evaluated without making any strong assumption on the K content of the primitive mantle. To remove the potassium concentrations from equation (5.1), one can use the calculation of excess argon introduced by Coltice *et al.* (2000a) as

$$^{40}\text{Ar}^{\text{xs}} = ^{40}\text{Ar} - ^{40}\text{K}R(e^{\lambda T} - 1). \quad (5.2)$$

The excess argon expresses the degree of decoupling between potassium and argon in a reservoir, which is essentially due to degassing of K-bearing rocks. A negative  $^{40}\text{Ar}^{\text{xs}}$  is associated with a degassed reservoir, a zero value corresponds to a closed system and a positive value is associated with a gas-rich (or potassium poor) reservoir, such as the atmosphere. Equation (5.1) then becomes

$$^{40}\text{Ar}_{\text{Atm+CC}}^{\text{xs}} + ^{40}\text{Ar}_{\text{SM}}^{\text{xs}} + ^{40}\text{Ar}_{\text{DM}}^{\text{xs}} = 0 \quad (5.3)$$

and expresses the balance of the excess argon at the surface of the Earth (atmosphere plus continental crust) and the deficit argon in the silicate mantle (divided in distinctive shallow and deep regions).

The amount of excess argon in the crust–atmosphere system is close to  $1.9 \times 10^{16}$  kg (see Coltice *et al.* 2000a). The deficit of  $^{40}\text{Ar}$  in the shallow mantle cannot be determined accurately, since its  $^{40}\text{Ar}$  and K contents are not well documented. The estimate used previously, based on the popping rock, suggests that the shallow-mantle concentration of  $^{40}\text{Ar}$  is  $50\text{--}200 \times 10^{-12}$  mol  $\text{g}^{-1}$ . The shallow-mantle concentration of potassium probably lies between 30 and 80 ppm (Jochum *et al.* 1983). Varying these parameters as well as the extent of the shallow mantle provides the range of  $^{40}\text{Ar}_{\text{DM}}^{\text{xs}}$  depicted in figure 5. Because of the large uncertainties in the shallow-mantle concentrations, there cannot be a unique interpretation of the nature of the deep mantle:  $^{40}\text{Ar}_{\text{DM}}^{\text{xs}}$  can be zero, corresponding to a closed system (undegassed?), but, in the range of parameters,  $^{40}\text{Ar}_{\text{DM}}^{\text{xs}}$  can also correspond to a degassed or ‘overgassed’ deep mantle. In this framework, a degassed deep mantle is certainly as reasonable to conceive as a primitive undegassed one. Moreover, the popping rock  $^4\text{He}/^{40}\text{Ar}$  value of 1.5 is similar to that of the closed-system (as discussed above), although we note that the excess amount of  $^{40}\text{Ar}$  in the shallow mantle could be very small, leaving the deep mantle with an argon deficit close to  $-1.9 \times 10^{16}$  kg.

Even avoiding K/U uncertainties, the budget of argon in the various reservoirs cannot be decoupled from that of potassium. This budget is probably not a strong constraint on mantle models, and considerable improvement in our knowledge of shallow-mantle concentrations is needed. In this framework, a hypothetical reservoir the size of  $D''$  (*ca.*  $2 \times 10^{23}$  kg), made of 2.5 billion-year-aged oceanic crust and containing 600 ppm of potassium, would provide a value of  $-1.2 \times 10^{16}$  kg for  $^{40}\text{Ar}_{\text{DM}}^{\text{xs}}$ . This would imply an  $\text{Ar}^{\text{xs}}$  of  $-0.7 \times 10^{16}$  kg for the whole mantle except  $D''$ , which, for example, could be explained by rather uniform K and  $^{40}\text{Ar}$  concentrations of 50 ppm and  $120 \times 10^{-12}$  mol  $\text{g}^{-1}$ .

## 6. A recycling model of the mantle

The isotopic and trace-element compositions in OIBs show that the sources of plumes are often derived from sections of ancient oceanic crust. Every petrological unit observed on the ocean floor has been identified: pelagic sediments (Blichert-Toft *et al.* 1999a); plateaux (Gasperini *et al.* 2000); extrusive sections (sometimes altered) and gabbros (Hauri & Hart 1993; Eiler *et al.* 1996; Chauvel & Hémond 2000). The source of mantle plumes is then made from poorly mixed subducted oceanic plates. Proposing that the ‘primitive’-like noble-gas signature is explained by recycling the peridotitic part of convective downwellings is consistent with the presence of slab material in plumes.

Segregation of the dense eclogitic oceanic crust at the base of the mantle is a mechanism that could provide the recycled components in the plume source, poor mixing in the boundary layer and deep chemical layering. The mineralogical assemblages in the basaltic crust at lower-mantle conditions have an excess density of a few per cent relative to the bulk mantle (Kesson *et al.* 1994). Convection calculations show that segregation would produce an accumulation of eclogite at the base of the mantle and a dense layer could grow with time according to a dynamic equilibrium between segregation due to gravity and plume entrainment (Christensen & Hofmann 1994). The heat-producing elements are concentrated in the oceanic crust and potentially destabilize the dense units. However, Christensen & Hofmann (1994) have performed convection calculations where the radioactive elements are confined

in the dense crust, corresponding to 5–20 times primitive mantle concentrations, and they conclude that ‘the heating of the bottom pools from within does not play a dominant role’. They only observed slight differences in the amount of segregation.

Separation of the crustal component at the base of the mantle should satisfy mass balance of trace elements, especially if sediments and plume products are considered (Coltice & Ricard 1999). The size of the layer formed would then be comparable to that of  $D''$ , which is known to be chemically distinct from the overlying mantle (Wysession 1996). Like partial melting, segregation is a process of chemical differentiation that sustains heterogeneity within the mantle. In the first investigation of this model (Coltice & Ricard 1999), the partly degassed peridotite was considered as a reservoir in order to perform box-model calculations. However, the recycling model only requires that the source of plumes is less mixed than the shallow mantle. The differences between results from Coltice & Ricard (1999) and the present studies can be mostly attributed to the limitations of box models in accounting for mixing heterogeneities (Coltice *et al.* 2000).

## 7. Conclusions

The ‘primitive’-like noble gases observed in Hawaiian and Icelandic samples contain indications of whether or not there exists a geochemically primitive layer in the deep mantle. If one exists, mass balance implies that the fraction of primitive material in these hotspots is very low and therefore, except for rare gases, incompatible elements in OIBs and MORBs should be similar. It also implies that  $^3\text{He}$  composition in the primitive mantle is richer than in carbonaceous chondrites. Furthermore, the primitive-layer hypothesis requires that helium and neon should not have been fractionated by extensive degassing of the shallow mantle, which is very unlikely.

On the contrary, partly degassed peridotite, observed in the shallow mantle, can account for the source of ‘primitive’-like noble-gas OIBs, considering isotopic ratios and  $^3\text{He}/^{22}\text{Ne}$  data. The peridotite and recycled oceanic crust are ubiquitous components in the mantle, well mixed in the shallow part and poorly mixed in the deep thermal boundary layer. These peridotites most likely contain some veins of primitive material. In this model, ‘primitive’-like plumes would carry the same concentrations of  $^3\text{He}$ ,  $^{22}\text{Ne}$  or  $^{36}\text{Ar}$  as the shallow mantle. No specific assumptions on the relative compatibility of helium and uranium have been used to reach these conclusions. The mechanism for separating peridotitic and crustal components in the boundary layer tapped by plumes can be the gravitational segregation of the denser oceanic crust at the bottom of the mantle. This model would provide a deep layer of recycled components, corresponding to the extent of the  $D''$  layer. The chemical heterogeneity of the mantle could then be a consequence of the combination of plate tectonics and petrological density differences.

## References

- Albarède, F. 1998 Time-dependent models of U–Th–He and K–Ar evolution and the layering of mantle convection. *Chem. Geol.* **145**, 413–429.
- Allègre, C. J. & Turcotte, D. L. 1986 Implications of a two component marble-cake mantle. *Nature* **323**, 123–127.
- Allègre, C. J., Hofmann, A. W. & O’Nions, R. K. 1996 The argon constraints on mantle structure. *Geophys. Res. Lett.* **23**, 3555–3557.

- Anderson, D. L. 1998 A model to explain the various paradoxes associated with mantle noble gas geochemistry. *Proc. Natl Acad. Sci. USA* **95**, 9087–9092.
- Ballentine, C. J. & Barfod, D. N. 2000 The origin of air-like noble gases in MORB and OIB. *Earth Planet. Sci. Lett.* **180**, 39–48.
- Blichert-Toft, J., Frey, F. A. & Albarède, F. 1999a Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts. *Science* **285**, 879–882.
- Blichert-Toft, J., Albarède, F. & Kornprobst, J. 1999b Lu–Hf isotope systematics of garnet pyroxenites from Beni Bousera, Morocco: implications for basalt origin. *Science* **283**, 1303–1306.
- Bunge, H.-P., Richards, M. A., Lithgow-Bertelloni, C., Baumgardner, J. R., Grand, S. P. & Romanowicz, B. A. 1998 Time scales and heterogeneous structure in geodynamic Earth models. *Science* **280**, 91–95.
- Chauvel, C. & Hémond, C. 2000 Melting of a complete section of recycled oceanic crust: trace element and Pb isotopic evidence from Iceland. *Geochem. Geophys. Geosyst.* **1**, 1999GC000003.
- Christensen, U. R. & Hofmann, A. W. 1994 Segregation of subducted oceanic crust in the convecting mantle. *J. Geophys. Res.* **99**, 19 867–19 884.
- Coltice, N. & Ricard, Y. 1999 Geochemical observations and one layer mantle convection. *Earth Planet. Sci. Lett.* **174**, 125–137.
- Coltice, N., Albarède, F. & Gillet, Ph. 2000a  $^{40}\text{K}$ – $^{40}\text{Ar}$  constraints on recycling continental crust into the mantle. *Science* **288**, 845–847.
- Coltice, N., Ferrachat, S. & Ricard, Y. 2000b Box modeling the chemical evolution of geophysical systems: case study of the Earth's mantle. *Geophys. Res. Lett.* **27**, 1579–1582.
- Davies, G. F. 1981 Earth's neodymium budget and the structure and evolution of the mantle. *Nature* **290**, 208–213.
- Dixon, E., Honda, M., McDougall, I., Campbell, I. & Sigurdsson, I. 2000 Preservation of near-solar isotopic ratios in Icelandic basalts. *Earth Planet. Sci. Lett.* **180**, 309–324.
- Eiler, J. M., Farley, K. A., Valley, J. M., Hofmann, A. W. & Stolper, E. M. 1996 Oxygen isotope constraints on the sources of Hawaiian volcanism. *Earth Planet. Sci. Lett.* **144**, 453–468.
- Eiler, J. M., Schiano, P., Kitchen, N. & Stolper, E. M. 2000 Oxygen-isotope evidence for recycled crust in the sources of mid-ocean ridge basalts. *Nature* **403**, 530–534.
- Farley, K. A. & Poreda, R. J. 1993 Mantle neon and atmospheric contamination. *Earth Planet. Sci. Lett.* **114**, 325–339.
- Farley, K., Maier-Reimer, E., Schlosser, P. & Broecker, W. S. 1995 Constraints on  $^3\text{He}$  fluxes and deep-sea circulation from an oceanic general circulation model. *J. Geophys. Res.* **100**, 3829–3839.
- Ferrachat, S. & Ricard, Y. 2001 Mixing properties in the Earth's mantle: effects of the viscosity stratification and of oceanic crust segregation. *Geochem. Geophys. Geosyst.* **2**, 2000GC000092.
- Gasperini, D., Blichert-Toft, D., Bosh, A., Del Moro, P., Macera, P., Télouk, F. & Albarède, F. 2000 Evidence from Sardinian basalt geochemistry for recycling plume heads into the Earth's mantle. *Nature* **408**, 701–704.
- Grand, S. P. 1987 Tomographic inversion for shear velocity beneath the North American plate. *J. Geophys. Res.* **92**, 14 065–14 090.
- Halliday, A. N., Lee, D. C., Tommasini, S., Davies, G. R., Paslick, C. R., Fitton, J. G. & James, D. E. 1995 Incompatible trace elements in OIB and MORB and source enrichment in the sub-oceanic mantle. *Earth Planet. Sci. Lett.* **133**, 379–395.
- Hanyu, T. & Kaneoka, I. 1997 The uniform and low  $^3\text{He}/^4\text{He}$  ratios of HIMU basalts as evidence for their origin as recycled materials. *Nature* **390**, 273–276.
- Harper Jnr, C. L. & Jacobsen, S. B. 1996 Noble gases and Earth's accretion. *Science* **273**, 1814–1818.
- Harrison, D. W., Burnard, P. G. & Turner, G. 1999 Noble gas behavior and composition in the mantle: constraints from the Iceland plume. *Earth Planet. Sci. Lett.* **171**, 199–207.

- Hauri, E. E. & Hart, S. R. 1993 Re–Os isotope of HIMU and EMII OIBs from the South Pacific Ocean. *Earth Planet. Sci. Lett.* **114**, 426–436.
- Hofmann, A. W. 1988 Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.* **90**, 297–314.
- Hofmann, A. W. 1997 Mantle geochemistry: the message from oceanic volcanism. *Nature* **385**, 219–229.
- Honda, M. & Patterson, D. B. 1999 Systematic elemental fractionation of mantle-derived helium, neon, and argon in mid-oceanic ridge glasses. *Geochim. Cosmochim. Acta* **63**, 2862–2874.
- Jacobsen, S. B. & Wasserburg, G. J. 1979 The mean age of mantle and crustal reservoirs. *J. Geophys. Res.* **84**, 7411–7427.
- Jean-Baptiste, P. 1992 Helium-3 distribution in the deep world ocean. In *Isotopes of noble gases as tracers in environmental studies. Proc. Consultants Meeting, International Atomic Energy Agency, Vienna*, pp. 219–240.
- Jochum, K. P., Hofmann, A. W., Ito, E., Seufert, H. M. & White, W. M. 1983 K, U and Th in mid-ocean ridge basalt glasses and heat production. *Nature* **306**, 431–436.
- Kellogg, L. H., Hager, B. H. & van der Hilst, R. D. 1999 Compositional stratification in the deep mantle. *Science* **283**, 1881–1884.
- Kesson, S. E., Fitz Gerald, J. D. & Shelley, J. M. G. 1994 Mineral chemistry and density of subducted basaltic crust at lower mantle pressure. *Nature* **37**, 767–769.
- Kurz, M. D., Jenkins, W. J. & Hart, S. R. 1982 Helium isotopic systematics of oceanic island and mantle heterogeneity. *Nature* **297**, 43–47.
- McDonough, W. F. & Sun, S. 1995 The composition of the Earth. *Chem. Geol.* **120**, 223–253.
- Mazor, E., Heymann, D. & Anders, E. 1970 Noble gases in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **34**, 781–824.
- Moreira, M. & Sarda, P. 2000 Noble gas constraints on degassing processes. *Earth Planet. Sci. Lett.* **176**, 375–386.
- Moreira, M., Kunz, J. & Allègre, C. J. 1998 Rare gas systematics in popping rock: isotopic and elemental compositions in the upper mantle. *Science* **279**, 1178–1181.
- Moreira, M., Breddam, K., Curtice, J. & Kurtz, M. D. 2001 Solar neon in the Icelandic mantle; new evidence for an undegassed lower mantle. *Earth Planet. Sci. Lett.*, **185**, 15–23.
- Pearson, D. G., Davies, G. R., Nixon, P. H., Greenwood, P. B. & Matthey, D. P. 1991 Oxygen isotope evidence for the origin of pyroxenites in the Beni Bousera peridotite massif, North Morocco: derivation from subducted oceanic lithosphere. *Earth Planet. Sci. Lett.* **102**, 289–301.
- Pepin, R. O., Palma, R. L. & Schlutter, D. J. 2001 Noble gases in interplanetary dust particules. II. Excess  $^3\text{He}$  in cluster particules and modelling constraints on IDP exposures to cosmic ray irradiation. *Meteoritics Planet. Sci.* **36**, 1515–1534.
- Porcelli, D. & Wasserburg, G. J. 1995 Mass transfer of helium, neon, argon, and xenon through a steady-state upper mantle. *Geochim. Cosmochim. Acta* **59**, 4921–4937.
- Ricard, Y., Richards, M. A., Lithgow-Bertelloni, C. & LeStunff, Y. 1993 A geodynamic model of mantle density heterogeneity. *J. Geophys. Res.* **98**, 21 895–21 909.
- Sarda, P., Staudacher, T. & Allègre, C. J. 1988 Neon isotopes in submarine basalts. *Earth Planet. Sci. Lett.* **91**, 73–88.
- Sarda, P., Moreira, M. & Staudacher, T. 1999 Argon-lead isotopic correlation in mid-Atlantic ridge basalts. *Science* **283**, 666–668.
- Sims, K. W. & De Paolo, D. J. 1997 Inferences about mantle magma sources from incompatible element concentration ratios in oceanic basalts. *Geochim. Cosmochim. Acta* **61**, 765–784.
- Stuart, F. M. & Grenville, T. 1998 Mantle derived  $^{40}\text{Ar}$  in mid-ocean ridge hydrothermal fluids: implications for the source of volatiles and mantle degassing rates. *Chem. Geol.* **147**, 77–88.
- Trieloff, M., Kunz, J., Clague, D. A., Harrison, D. & Allègre, C. J. 2000 The nature of pristine noble gases in mantle plumes. *Science* **288**, 1036–1038.

- Turner, G. 1989 The outgassing history of the Earth's atmosphere. *J. Geol. Soc. Lond.* **146**, 147–154.
- Tyburczy, J. A., Frisch, B. & Arhens, T. J. 1986 Shock-induced volatile loss from a carbonaceous chondrite: implications for planetary accretion. *Earth Planet. Sci. Lett.* **80**, 201–207.
- Valbracht, P. J., Staudacher, T., Malahoff, A. & Allègre, C. J. 1997 Noble gas systematics of deep rift zone glasses from Loihi seamount, Hawaii. *Earth Planet. Sci. Lett.* **150**, 399–411.
- van der Hilst, R. D., Widiyantoro, S. & Engdahl, E. R. 1997 Evidence for deep mantle circulation from global tomography. *Nature* **386**, 578–584.
- van Keken, P. E. & Ballentine, C. J. 1998 Whole-mantle versus layered convection and the role of a high-viscosity lower mantle in terrestrial volatile evolution. *Earth Planet. Sci. Lett.* **156**, 19–32.
- Wyssession, M. E. 1996 Continents of the core. *Nature* **381**, 373–375.
- Yatsevich, I. & Honda, M. 1997 Production of nucleogenic neon in the Earth from natural radioactive decay. *J. Geophys. Res.* **102**, 10 291–10 298.
- Zindler, A. & Hart, S. 1986 Chemical geodynamics. *A. Rev. Earth Planet. Sci.* **14**, 493–571.