

## The helium paradoxes

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**ABSTRACT** The ratio  $^3\text{He}/^4\text{He}$  (R) plays a central role in models of mantle evolution that propose an undegassed lower mantle, rich in the primordial isotope  $^3\text{He}$ . A large primordial volatile-rich reservoir, a feature of recent models, is inconsistent with high-temperature accretion and with estimates of crustal and bulk Earth chemistry. High R can alternatively reflect high integrated  $^3\text{He}/(\text{U}+\text{Th})$  ratios or low  $^4\text{He}$  abundances, as expected in refractory portions of the upper mantle. I show that high R materials are gas-poor and are deficient in radiogenic  $^4\text{He}$  compared with midocean ridge basalts. The seemingly primitive (i.e., high R) signatures in “hotspot” magmas may be secondary, derived from  $\text{CO}_2$ -rich gases, or residual peridotite, a result of differential partitioning of U and He into magmas. A shallow and low  $^3\text{He}$  source explains the spatial variability and the temporal trends of R in ocean islands and is consistent with a volatile-poor planet. A shallow origin for the “primitive” He signature in ocean island basalts, such as at Loihi, reconciles the paradoxical juxtaposition of crustal, seawater, and atmospheric signatures with inferred “primitive” characteristics. High  $^{238}\text{U}/^{204}\text{Pb}$  components in ocean island basalts are generally attributed to recycled altered oceanic crust. The low  $^{238}\text{U}/^3\text{He}$  component may be in the associated depleted refractory mantle. High  $^3\text{He}/^4\text{He}$  ratios are due to low  $^4\text{He}$ , not excess  $^3\text{He}$ , and do not imply or require a deep or primordial or undegassed reservoir.  $^{40}\text{Ar}$  in the atmosphere also argues against such models.

Current views of the Earth’s interior are contradictory. Geochemical box modelers favor a layered mantle with a primordial gas-rich lower mantle (PM) and a depleted upper mantle (DUM), the residue of crustal extraction (1–3). DUM is the presumed source of midocean ridge basalts (MORBs), and PM is the source of ocean island basalts (OIBs). Some models (“steady state”) invoke a balance between radioactive heat production and surface heat flow (2) and between flux of noble gases into the upper mantle from below and out at ridges (3, 4). Mantle degassing models have been postulated where all primordial noble gases reside in the lower mantle (equated with the OIB source region) and are transferred into the upper mantle by plumes (2–4). The higher  $^4\text{He}/^3\text{He}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios of MORBs are attributed to the accumulation of  $^4\text{He}$  and  $^{21}\text{Ne}$  during residence in the upper mantle for periods of  $\approx 1$  Ga ( $10^9$  years). In these models, it is a mystery how a large primitive reservoir could have accreted and have been preserved against degassing during accretion, core formation, and mantle convection (5–7). On the other hand, small amounts of  $^3\text{He}$  in the mantle can be explained in various ways.

A completely different kind of model is suggested by the physics of accretion and acknowledgment of the high-temperature beginnings of the Earth (7). The Earth melts, differentiates, and degasses further during accretion. Radioactivity is only part of the thermal budget; there cannot be an

instantaneous balance between heat productivity and heat flow (6). This means that there is less U and K (and  $^4\text{He}$ ,  $^{40}\text{Ar}$ ,  $^{206}\text{Pb}$ , etc.) remaining in the mantle than assumed in the primordial mantle models. The outer parts of the Earth are enriched in incompatible and volatile elements. Most of the mantle is depleted, degassed, and refractory (8). There is growing acceptance of the idea (8, 9) that most or all of the mantle has been processed (7, 9–12), to form the crust and the MORB reservoir, or MORB mantle (MM). There is no evidence from other isotopic systems for a primitive component in OIBs. Regions with high ratio  $^3\text{He}/^4\text{He}$  (R) basalts also generally have low R basalts as well (13).

In spite of its high temperature accretion, the Earth contains  $^3\text{He}$  and other primordial gases. The mechanisms by which the noble gases are trapped in the Earth are unknown, but suggestions range from solubility in a magma ocean (5) to accretion of a late veneer, after the bulk of the Earth has accreted (14). The amount of  $^3\text{He}$  in the Earth is unconstrained. It is not the purpose of this article to discuss the mechanism by which noble gases are brought into the Earth but only to discuss the processes that give variations in the Rs of basalts. It is concluded, however, that the amount of  $^3\text{He}$  currently in the Earth may be very small, in contrast to most current models.

In most geochemical treatments, basalts with high R are viewed as having an “excess” of  $^3\text{He}$ . High R reflects high time-integrated  $^3\text{He}/(\text{U}+\text{Th})$  ratios (hereafter  $^3\text{He}/\text{U}$ ). Because  $^4\text{He}$  is a decay product of U, the high R reservoir may be deficient in U and, consequently,  $^4\text{He}$ . In this more general view, there is no need for a primordial undegassed reservoir but only a mantle that is heterogeneous in  $^3\text{He}/\text{U}$ . It has been known for some time (e.g., ref. 9) that the Earth is deficient in volatile and moderately volatile elements, such as Na, K, Rb, and C, compared with chondritic abundances. Current geochemical models introduce the paradox that He, one of the most volatile and hard to accrete elements, is less depleted in the Earth, relative to chondrites, than other volatile elements. In addition to the overall depletion of volatiles, there is evidence that most of the mantle has given up its large ion lithophile (LIL) to form the crust and upper mantle. The bulk of the mantle may, in fact, be extensively purged of LIL and volatile elements (7–9, 15) relative to the crust and shallow mantle. In the extreme case, all of the volatiles may have been brought to the Earth by the final 1–2% of accreted material, the late veneer (16). This late veneer hypothesis is favored if current models of temperatures in the solar nebula in the Earth accretion zone are valid; volatiles do not condense in this zone, they must be added from outer zones (7, 17). A volatile and LIL-depleted model for the bulk of the mantle, including the lower mantle, is the antithesis of models that invoke a primitive undegassed lower mantle. The late veneer hypothesis is attractive because it provides an explanation for solar or chondritic relative abundances of the noble metals and noble gases,

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Abbreviations: R, ratio  $^3\text{He}/^4\text{He}$ ; MORB, midocean ridge basalt; OIB, ocean island basalt; PM, primordial gas-rich lower mantle; DUM, depleted upper mantle; MM, MORB mantle.

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but the absolute abundances of the volatile elements is very low compared with the DUM/PM models.

Other reservoirs, invoked to explain some aspects of mantle geochemistry, are the lithosphere and the perisphere (18–20). The perisphere is a shallow region, one sink of incompatible material stripped from the slab by dehydration reactions (19) and residual melts and gases. Midplate volcanics pick up various geochemical signatures as they traverse the perisphere, lithosphere, and crust (18, 20). Tomography shows that slabs penetrate deep into the mantle but the very low velocities above slabs suggest that volatiles leave the slab at shallow depths (21). The shallow mantle is fluxed with fluids released by dehydration reactions and eclogitization, presumably with the enriched mantle (EM) EM1, EM2, and HIMU (i.e., enriched and high  $^{238}\text{U}/^{204}\text{Pb}$ ) components of the slab. Some of this material appears in island arc basalts, but some remains in the shallow mantle. The “purity” of depleted magmas is retained by bringing them to the surface at regions of thin lithosphere or where EM has been cleared out or depleted by previous magmatism (19). Depleted magmas may be due to the absence of the contaminating layer rather than universally DUM. In the plume model, the enriched and “undegassed” material is brought from the lower mantle to midplate volcanoes, through DUM. Plumes are treated as point sources of pollution. In the perisphere model, new rifts and newly extending lithosphere tap the enriched layer, and a transient period of extensive volcanism of enriched basalts ensues. Magma drainage is extremely rapid through the upper mantle and through narrow cracks (22). The transient emptying of ponded magma through lithospheric cracks is an alternate to the plume hypothesis, which assumes no melting in the absence of deep plumes. The asthenosphere is partially molten, even in the absence of lithospheric thinning or plumes (23) and the shallow mantle has the geochemical properties attributed to “plume mantle” (19).

In most geochemical models, the MORB reservoir occupies the whole upper mantle (DUM). It is a paradox that newly opening rifts do not provide MORBs and that extending terranes in general provide OIB-like basalts (19, 24). These observations imply a ready availability of enriched components, either as enriched plums (the plum pudding model) or a shallow enriched layer. In either case, it is only mature ridges that provide typical MORBs. Regions of the mantle that have not recently experienced melt extraction, or ridge processing, such as Hawaii, are expected to provide enriched melts from the shallow mantle (25). In the plume models, all non-MORB material is brought into the shallow mantle from deep sources and it then spreads out laterally. The problem with this view is that there are so many “plumes” in the Atlantic that the entire asthenosphere should be enriched by plume heads and lateral transport, giving an enriched shallow mantle along the mid-Atlantic ridge system. This layer then must be attenuated or removed before MORBs can appear, making this similar to the perisphere and plum pudding models.

Midplate volcanoes can be explained by shallow processes, near-surface contamination, and recycling of near-surface materials. The only remaining generally accepted indicator of deep or primitive mantle is high R. In steady-state models,  $^3\text{He}$  leaks into DUM from a gas-rich lower mantle (2–4). The mantle, however, was probably depleted and degassed, early and extensively, during the accretion process (7–10)—the DEE model. Volatiles and other incompatible elements were trapped in the upper mantle in early Earth history (8) or were brought in by a late veneer (16). In this model, the outer Earth is always enriched in incompatible elements compared with deeper mantle. Crust extraction depletes the large-ion elements relative to compatible elements and the MM is depleted in this relative sense. In some models, the “depleted upper mantle” was formed by removal of the continental crust, leaving a residue that contains less U, Th, and K than PM (1,

26). A more complete mass balance model requires depletion of all of the mantle (DEE model) to satisfy crustal and MORB concentrations of the incompatible elements (8–12). Recycling returns enriched materials (sediments, altered crust) from the surface to the shallow mantle. The slab is likely the source of metasomatizing fluids, which permeate the shallow mantle. Gases exsolved from saturated magmas may be one source of the  $\text{CO}_2$ -rich metasomatizing fluids that are so prevalent in the shallow mantle. Because He is a neutral small-radius atom, it is not obvious that it should be more incompatible in crystals, relative to melts, than U and Th. Refractory residues or cumulates may, therefore, have high He/U ratios compared with basalts, and this is increased further by any trapping of exsolved volatiles.

The idea that crystal–melt partitioning may be responsible for U/He variations has been proposed before (13, 27). A more effective mechanism may be melt–vapor partitioning. U and Th prefer the melt, whereas  $\text{CO}_2$  and the noble gases prefer the vapor. Exsolution occurs upon magma ascent and trapping of vapor in cumulates or residual peridotite will decrease the U/He ratio, and ultimately, the R in shallow refractory portions of the mantle. Because He is more soluble in magma than the heavier noble gases, gas-filled inclusions made by this mechanism, and any magmas that inherit these inclusions upon ascent, will have low He/Ar and He/Ne ratios compared with the degassed magma. OIBs have this characteristic relative to MORBs.

### Noble Gases

R has been extensively used as a constraint on mantle stratigraphy. The underlying assumption is that high R means high  $^3\text{He}$ . Basalts and gases with high R have been attributed to a deep PM, whereas low R has been attributed to DUM or recycled crust (4, 28). The conjectured undegassed PM is ancient, has high contents of  $^3\text{He}$  and U, and has generated large quantities of  $^4\text{He}$  (3). It is predicted to provide much more  $^3\text{He}$  to the atmosphere than midocean ridges (2, 3). This is a testable prediction. It is a problem that high R basalts have very low concentrations of  $^3\text{He}$  and  $^4\text{He}$  and that ridges dominate the  $^3\text{He}$  volatile flux. High R basalts could be derived from sources with little ingrown  $^4\text{He}$  instead of having an  $^3\text{He}$  excess. This alternative, which has not been previously discussed, would require a drastic revision in views of mantle stratigraphy and evolution and in the assumptions and nomenclature (“undegassed reservoir,” “primordial mantle,” and “degassed upper mantle”) of noble gas geochemistry.

MORBs, which are generally thought to be from “the degassed reservoir,” actually have higher concentrations of  $^3\text{He}$ ,  $^4\text{He}$ ,  $^{40}\text{Ar}$ ,  $^{21}\text{Ne}$ , and  $^{136}\text{Xe}$  than OIB samples (29–36), even those with the highest Rs.  $^3\text{He}$  abundances of ridge basalts are usually orders of magnitude greater than hotspot basalts. This is a long-standing paradox in the standard model. Even some mantle xenoliths have much higher  $^3\text{He}$  concentrations than high R basalts (31, 37, 38), and this gas is clearly secondary. The low abundances of the noble gases including  $^3\text{He}$  in OIBs can be interpreted in several different ways: (i) The source region for OIBs is not a primitive reservoir. (ii) High R implies high He/U, not high (“excess”)  $^3\text{He}$ . (iii) OIBs are more degassed than MORBs (26–29).

It is difficult to infer the volatile contents of magmas and their source regions because of shallow degassing effects. MM is generally thought to be volatile depleted because of the low concentrations of water and moderately volatile elements. MORBs, however, are  $\text{CO}_2$ -rich, as well as rich in noble gases, and the inferred source region may be very  $\text{CO}_2$ -rich (39–41). Because  $\text{CO}_2$  is the main carrier phase for He and He has higher solubilities in magma than other noble gases, the behavior of  $\text{CO}_2$  and He in MORBs may differ from that of  $\text{H}_2\text{O}$  and other volatiles.  $\text{CO}_2$  exsolves and is trapped at

different depths and mechanisms than H<sub>2</sub>O. It is sometimes assumed that because MORBs have low water contents, it must come from a degassed reservoir. The same sort of logic, applied to the noble gases, would say that the OIB reservoir is depleted in volatile elements. However, one must be cautious before generalizing in this way.

In this article, I investigate the possibility that the absolute and relative abundances of the gases in MORBs, OIBs, and xenoliths are controlled by solubility, melt–gas equilibration, and melt–gas separation, in addition to solid–melt partitioning. Degassed magmas in this situation should have high <sup>4</sup>He/<sup>40</sup>Ar and <sup>4</sup>He/<sup>21</sup>Ne ratios because of the high solubility of He in the melt (32–36). OIB samples usually have lower ratios than MORBs, suggesting that MORBs are more degassed than OIBs (Table 1), the opposite of the standard assumption. Most MORBs have lost more than 90% of their gases prior to eruption (33). Nevertheless, the <sup>4</sup>He contents of MORBs are much greater than OIBs, and <sup>3</sup>He/U ratios imply retention of a large fraction of the radioactive decay products of U and Th (14, 41). The MORB reservoir apparently is gas-rich, both in absolute and relative terms, and may be ancient.

If OIBs are degassed before sampling, they should be low in all the noble gases, but they are enriched in <sup>36</sup>Ar and <sup>84</sup>Kr compared with MORBs. These are the isotopes for which seawater contamination is most likely (32, 34). OIBs appear to be extensively contaminated by atmospheric or seawater gases (32, 34, 42, 43).

There are various tests of the hypothesis that high R basalts have low <sup>3</sup>He contents (in spite of their assumed <sup>3</sup>He “excess”) because they have been more extensively degassed at shallow depth than MORBs: (i) A degassed melt should have higher He/Ar, He/Ne, and He/CO<sub>2</sub> ratios than the exsolved gas or than an undegassed melt. (ii) A primitive reservoir should contain primitive (solar?) ratios of <sup>3</sup>He/<sup>22</sup>Ne; degassed melts should carry higher ratios. (iii) Degassing of <sup>3</sup>He to the atmosphere should be dominated by the hotspot flux, not by the ridge flux (2).

The remainder of this article discusses various tests of the hypothesis that high R implies excess <sup>3</sup>He rather than low U. The above tests do not support the hypothesis that OIBs are, or were, rich in <sup>3</sup>He compared with MORBs, or that they tap a relatively undegassed or lower mantle reservoir. Deep samples of high R glasses are now available and they also have low <sup>3</sup>He contents compared with MORBs (see below).

Table 1. He content and isotopic ratios of MORB or MM and “primordial” or “plume” material (PM)

|  | MM                                     | PM                       | Ref(s).                  |
|--|--|--------------------------|--------------------------|
| <sup>3</sup> He/ <sup>4</sup> He                       | 6 to 10 R <sub>a</sub><br>(definition) | 2 to 31 R <sub>a</sub>   | 28, 32                   |
| <sup>3</sup> He/ <sup>36</sup> Ar                      | 2                                      | 1†                       | 32                       |
| <sup>3</sup> He/ <sup>130</sup> Xe                     | 4.5                                    | 1†                       | 32                       |
| <sup>3</sup> He/ <sup>22</sup> Ne                      | 4                                      | 1†                       | 32                       |
|  | 1.6                                    | 1†                       | 45                       |
| He/Sr  | 7                                      | 1†                       | 8, 31                    |
| <sup>3</sup> He/CO <sub>2</sub> (×10 <sup>-10</sup> )  | 1.3 to 10                              | 0.5 to 5                 | 37                       |
| <sup>4</sup> He/CO <sub>2</sub> (×10 <sup>-5</sup> )   | 1 to 20                                | 0.3 to 2                 | 37                       |
| He, μcc/g  | 1 to 80                                | 0.03 to 4.5              | 33, 34, 43<br>46, 47, 53 |
| <sup>3</sup> He, ncc/g                                 | 0.01 to 1                              | 10 <sup>-4</sup> to 0.04 | 33, 34, 43<br>46, 47     |
| <sup>3</sup> He/ <sup>238</sup> U (atomic ratio)       | 10 <sup>-4</sup>                       | 4.5 × 10 <sup>-4</sup>   | 32                       |
| <sup>4</sup> He*/ <sup>21</sup> Ne* (10 <sup>7</sup> ) | >4                                     | >3                       | 4, 5, 42, 45             |
| <sup>4</sup> He*/ <sup>40</sup> Ar* (10 <sup>7</sup> ) | >1                                     | >3                       | 4, 5, 42<br>43, 46       |

\*Radiogenic or nucleogenic component.

†Reference value.

## High <sup>3</sup>He or Low <sup>4</sup>He?

Table 1 summarizes ratios of He to other noble gases and CO<sub>2</sub>. Results under MM are for MORBs or the inferred MORB reservoir (32). MM is often referred to as the outgassed reservoir or, in the geochemical literature, the upper mantle or DUM (30, 32). It is preferable to use a neutral, rather than a model-dependent, designation. <sup>3</sup>He/CO<sub>2</sub> ratios are indistinguishable between ridge and hotspot magmas but <sup>4</sup>He/CO<sub>2</sub> ratios tend to be higher for MORBs (37). The only ratios that could imply “excess” <sup>3</sup>He are R and <sup>3</sup>He/<sup>238</sup>U (32). High <sup>238</sup>U implies high <sup>4</sup>He because the latter is the decay product of the former. High <sup>238</sup>U/<sup>3</sup>He (ν or NU) is just the characteristic required to explain the low values of R of MORBs, relative to Loihi and other OIBs by high <sup>4</sup>He instead of low primordial gas content.

Noble gases in OIBs are often interpreted as mixtures of MORB gases, atmosphere, and a variable component that can be high or low in R (28, 30–32). Mixing calculations allow one to estimate the properties of the end members (32). Noble gas characteristics of MORBs or MM and OIBs or the so-called plume (PM) end-members are summarized in Table 1. The ratios <sup>3</sup>He/<sup>22</sup>Ne, <sup>3</sup>He/<sup>36</sup>Ar, and <sup>3</sup>He/<sup>130</sup>Xe are all low in PM relative to MM. Atmospheric contamination is apparent for ratios involving heavy noble gases. The “primordial” reservoir, and Loihi basalts are, paradoxically, deficient in <sup>3</sup>He compared with MORBs and the “degassed” reservoir, both in absolute abundances and relative to other gases. <sup>4</sup>He increases with time from the radioactive decay of U and Th; these latter elements are geochemically distinct from <sup>3</sup>He and fractionate easily from it. Mixing hyperbole involving He and Sr or Pb isotopes imply He/Sr and He/Pb ratios lower in the PM end-member than in the MM end-member, inconsistent with PM being undegassed (8, 31, 44). The conclusion is that MM is “enriched” in <sup>3</sup>He compared with the “undegassed” reservoir. This is a paradox for the primordial mantle model.

These results are all consistent with low R being the result of high <sup>4</sup>He contents. This implies that MM has higher U and Th contents than PM or is older. The amount of <sup>4</sup>He in MORB glasses and the inferred <sup>4</sup>He content of MM, in fact, require a substantial time interval to accumulate (34, 35). If the MORB reservoir has been depleted (low U) and degassed, it should be low in <sup>3</sup>He and <sup>4</sup>He. It is not. The <sup>206</sup>Pb content of MORBs, relative to <sup>238</sup>U, and “excess” <sup>129</sup>Xe also imply an ancient reservoir. Many MORB samples fall near the geochron; few OIB samples do.

One does not know, à priori, what should be the ratios of the above isotopes in a primitive undegassed reservoir. The stable isotopes should occur in high concentrations, by definition of “undegassed,” but daughter products such as <sup>4</sup>He, <sup>21</sup>Ne, and <sup>40</sup>Ar should also be high because a primordial reservoir is both old and undepleted in U and K and is undegassed. Calculations show that if high R basalts originally had high <sup>3</sup>He and <sup>4</sup>He, rather than low <sup>4</sup>He, their reservoir should contain approximately chondritic abundances of the noble gases (3), making Earth a gas-rich planet. The evidence is, however, that Earth is a volatile-poor body (8, 13, 14), which favors the low <sup>4</sup>He option. These are among the various paradoxes associated with the standard noble gas model. The He and Ne in the mantle may have solar ratios (29, 36), but this does not mean that solar concentrations are expected because this would imply that the Earth accreted only from very small particles.

## Daughter Isotopes

The ratios of radiogenic or nucleogenic isotopes such as <sup>4</sup>He/<sup>40</sup>Ar and <sup>4</sup>He/<sup>21</sup>Ne are constraints on the sources of the gases in the so-called degassed and nondegassed reservoirs and on sources of contamination. These ratios in MORBs are

generally greater than theoretical production ratios, implying degassing fractionation.

$^4\text{He}$ ,  $^{21}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{244}\text{Pu}$ , and  $^{136}\text{Xe}$  are produced by U, Th, and K. For given K/U and Th/U ratios one can calculate production ratios (e.g., of  $^4\text{He}/^{40}\text{Ar}$ ,  $^4\text{He}/^{21}\text{Ne}$ , etc.) (3, 32, 34, 45). A primitive undegassed reservoir should have approximately these ratios. Ratios involving  $^{40}\text{Ar}$  and  $^{136}\text{Xe}$  in high R basalts are affected by atmospheric or seawater contamination (32) but then the question arises, why are basalts from a deep primordial reservoir most affected by shallow contamination? An outgassed reservoir should have low total abundances of the noble gases and  $^4\text{He}/^{21}\text{Ne}$  ratio close to the production ratio. MORB glasses, however, generally have  $^4\text{He}/^{21}\text{Ne}$  ratios of 2–10 times the theoretical production ratio (36, 43), consistent with He retention by a magma after several stages of degassing. “Popping rock” has elemental ratios consistent with much less degassing (46, 47). Many “hotspot” and non-MORB samples have  $^4\text{He}/^{21}\text{Ne}$  ratios much lower than the production ratio. Low values imply a gas source that is or was in equilibrium with a melt and are consistent with storage after degassing in a low U–Th environment. Vesicles in magmas, for example, have low ratios. Low ratios are also caused by atmospheric contamination, but they do not imply a melt that has been outgassed more thoroughly than MORBs, the conventional explanation of low  $^3\text{He}$  content of OIBs.

Summaries of  $^4\text{He}/^{40}\text{Ar}$  ratios (31, 46, 48) show that most MORB samples have ratios between 3 and 50 and that most “plume” samples range from 2 to less than 0.01. Many MORBs have  $^4\text{He}/^{40}\text{Ar}$  ratios of 10 to 20 times the equilibrium production range of 1.4 to 1.8. These results are consistent with “plume” gases being secondary. Most MORBs have lost considerable gas before sampling but are still gas-rich, implying a gas-rich MM, not a DUM source.

The solubility of He in basaltic magma is an order of magnitude higher than Ar (35, 49, 50) and also higher than  $\text{CO}_2$  and the heavy noble gases. As magmas degas, the residual fluid develops high He/Ar, He/Ne, and He/Xe ratios, and the gas develops complementary ratios. If the exsolved gas is collected and stored in a low U environment, it freezes in the R (51, 52). Degassing of MORBs probably starts at depths of order 60 km (47). Mantle xenoliths often contain higher noble gas concentrations than their host OIB magmas and may affect the noble gas isotopic characteristics of the magma.

Crystal–melt fractionation can also separate He from uranium and thorium (44). U and Th are large-radius large-charge ions and are not readily accommodated in crystalline lattices of normal mantle silicates. He is a small neutral atom and one expects the U/He ratios of melts to be higher than residual crystals. Therefore, both gas–melt and melt–crystal processes can fractionate He from U and Th, and therefore, R variations can be achieved by normal magmatic processes. Residual mantle (“restite”) or cumulates can be expected to have high He/U ratios and, with time, high Rs relative to fertile mantle.

### Solar Ratios

In addition to  $^4\text{He}/^{21}\text{Ne}$ , one can use the ratio  $^3\text{He}/^{22}\text{Ne}$  to test for OIB degassing. Ne isotopes in mantle-derived samples trend from the atmospheric  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio toward the solar (32, 42) or interplanetary dust particle value (14), which may represent the composition of Ne in the mantle. Solar-like Ne is evident in both MORB and Loihi basalts (32, 34). MORBs have  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios much higher than solar or Loihi, consistent with nucleogenic ingrowth of  $^{21}\text{Ne}$  in the MORB reservoir. MM is therefore ancient, undepleted (in U), or both. Neither the radiogenic nor the stable isotope ratios, He/Ne (Table 1), support the hypothesis that “primitive” high R basalts have low  $^3\text{He}$  because of extensive degassing relative to MORBs. The alternative conjecture that high R implies low  $^4\text{He}$  is supported by the data. High R, therefore, is not a

“primitive” signature nor does it imply derivation from an undegassed reservoir.

### Degassing and Mixing

The gas-rich popping rock found near  $14^\circ\text{N}$  along the mid-Atlantic ridge at a depth of 3.8 km has the highest  $^3\text{He}$  content found in any quenched magma (33, 47), including the more deeply derived high R Loihi glasses (53). It has  $^4\text{He}/^{40}\text{Ar}$  ratios close to production ratios and appears to be less degassed than other magmas. Degassing of such a magma will decrease the noble gas contents and increase the  $^3\text{He}/^{22}\text{Ne}$  and  $^4\text{He}/^{40}\text{Ar}$  ratios of the residual magma. Most MORBs have these characteristics compared with popping rock and can, therefore, be inferred to be degassed magmas. Mixing with air or seawater contaminated crust will decrease the  $^3\text{He}/^{22}\text{Ne}$ ,  $^4\text{He}/^{40}\text{Ar}$ ,  $^{21}\text{Ne}/^{22}\text{Ne}$ , and  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios. Loihi and other “hotspot” basalts have these characteristics, as well as low total  $^3\text{He}$  and  $^4\text{He}$  and high contents of the heavy noble gases, further indication of atmospheric contamination. The very low  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios found in Hawaiian OIBs, intermediate between MORB and atmospheric values, also suggest shallow contamination of OIBs. In addition to air and seawater, vesicles and fluid-filled inclusions are also potential sources of contaminating gases. Valbracht *et al.* (53) and Honda and McDougall (45) have suggested that MORB and Loihi basalts have  $^3\text{He}/^{22}\text{Ne}$  ratios of 9.4–11 and 6–7, respectively, both higher than the solar ratio of 3.6. This suggests that gas loss, followed by variable degrees of contamination, have been involved, with Loihi basalts (low total  $^3\text{He}$  and low  $^3\text{He}/^{22}\text{Ne}$  compared with MORBs) having the most extreme secondary characteristics. It also suggests that the Loihi source is not primordial (“solar”).

High R basaltic glasses ( $24\text{--}27 R_a$ ) have been obtained from depths of 3–5 km from the south rift of Loihi seamount (53). In spite of their great depth of quenching, these samples contain He at only 0.3–2.3  $\mu\text{cc/g}$ , about the same as surface samples, and 40–270 times less than MORB samples collected from shallower depths. Most of the He in these samples is in the matrix, not the vesicles, and the  $^3\text{He}/^{22}\text{Ne}$  ratios are less than in MORBs. This argues against more extensive degassing of the high R Loihi samples than the MORB samples and is consistent with a low  $^3\text{He}$  source. The very low  $^3\text{He}$  concentrations of Loihi and other high R basalts means they are susceptible to contamination by He sources in the shallow mantle and crust.

### Gas Emissions

If high R basalts have low total  $^3\text{He}$  because of eruptive or preruptive degassing, this gas should show up in hotspot gas emissions. In steady-state models (2, 3), hotspot flux is predicted to dominate the  $^3\text{He}$  loss of the mantle and may exceed the total ridge flux by an order of magnitude. Kilauea exhales 10 mol or less of  $^3\text{He}$  per year (54, 55), about 1% of the global total. Most of the rest is from ridges (55). Recent Kilauea magma eruption rates are  $>0.25 \text{ km}^3/\text{year}$  (56), more than 1% of the global midocean ridge rate of  $18 \text{ km}^3/\text{year}$ . There is therefore no excess  $^3\text{He}$  outgassed at Hawaii. The amount of  $^3\text{He}$  degassing from hotspots is trivial,  $<1\%$ , compared with that degassing from ocean ridges and island arcs (55). Paradoxically, there is more  $^3\text{He}$  outgassing at island arcs than at all hotspots combined. The low total  $^3\text{He}$  flux at hotspots is inconsistent with primordial gas-rich models of the Earth (2, 3) and with extensive gas loss from OIBs to explain low  $^3\text{He}$  abundances. By using He concentrations of popping rock (80  $\mu\text{cm}^3/\text{g}$ ) (33) and the production rate of oceanic crust, the global He outgassing rate corresponds to the complete outgassing of 3 km of such rock. The global  $^4\text{He}$  flux, however, is less than 10% of that expected from the heat flux associated with plate creation (57). This is the He-heat flow paradox. It

suggests that most MORBs have lost considerable gas before eruption. This gas loss may start near a depth of 60 km, a result of supersaturation, and the released CO<sub>2</sub>-He may end up, in part, in fluid inclusions in the shallow mantle (38, 53). This is consistent with the evidence for a much greater CO<sub>2</sub> content in the MORB reservoir than commonly assumed (39, 40). A high He content for MM is consistent with this and with the calculated <sup>4</sup>He build up from measured U (14, 41). O’Nions and Oxburgh (57) assume that He is lost and stored at a deep mantle boundary by some unspecified mechanism. The noble gas isotopic ratios favor a shallow melt-gas fractionation mechanism. High <sup>3</sup>He content of so-called primitive OIBs does not show up in the magmas or gaseous emissions, and there is no hint in other isotopic ratios that large He losses have occurred.

The He-heat flow paradox also indicates that noble gases are not as easily or efficiently outgassed, at the present time, as generally assumed. Magma must be brought to the very near surface before it can lose its gas to the atmosphere. Only about 10% of the <sup>4</sup>He that is being generated by radioactive decay is making its way to the Earth’s surface. In contrast, about 77% of the total <sup>40</sup>Ar ever made in the Earth resides in the atmosphere (8). The 77% figure for <sup>40</sup>Ar probably represents inefficient degassing rather than the presence of a completely undegassed reservoir. In some recent articles (4, 58), the missing <sup>40</sup>Ar is attributed to a primordial reservoir, rather than to incomplete extraction, as is clearly the case for <sup>4</sup>He.

## Summary

There is no support for the hypotheses that hotspots dominate the <sup>3</sup>He degassing budget of the Earth and that high R magmas are more extensively degassed than MORBs. There is therefore no support for the idea that high Rs imply an undegassed reservoir. The relatively high <sup>4</sup>He/<sup>21</sup>Ne, <sup>3</sup>He/<sup>22</sup>Ne, and <sup>4</sup>He/CO<sub>2</sub> ratios in MORBs suggest that it is the MORB reservoir that is He-rich and that the high R in MORBs is due to excess <sup>4</sup>He, not a deficit in the “primordial” isotope <sup>3</sup>He. The <sup>238</sup>U/<sup>206</sup>Pb ratio in some MORBs imply closed system evolution for nearly the age of the Earth. If MORBs are extensively degassed just before or during eruption, then the He age of the MORB reservoir (inferred from U/<sup>4</sup>He) is also comparable to the age of the Earth, and MM can be viewed as an ancient relatively undegassed reservoir, the opposite of the usual interpretation. This does not rule out extensive degassing of the mantle during accretion. The high content of <sup>4</sup>He and <sup>21</sup>Ne in MORBs, combined with estimates of <sup>238</sup>U contents in MORBs, imply that much of the radiogenic and nucleogenic gas generated over the age of the Earth in MM has been retained.

The amount of the <sup>40</sup>Ar in the atmosphere also suggests that <sup>40</sup>Ar has been retained. C is underabundant in the exosphere compared with other volatiles and it may also be retained in the mantle (39, 41). Missing volatiles do not necessarily imply the presence of a primordial reservoir, as usually assumed, but only inefficient extraction of gases or storage in the mantle as trapped degassed components.

Most of the characteristics of “hotspot” magmas such as isotopic chemistry (Sr, Nd, Pb, O, and C), oxidation state and noble gas abundance patterns are consistent with near-surface interactions or recycling, rather than with deep plumes and primordial mantle. The recognition that ocean island basalts are deficient in <sup>4</sup>He rather than enriched in <sup>3</sup>He means that there is no evidence for a primordial component in OIBs or for an undegassed reservoir. All of the characteristic geochemical signatures in OIBs can now be attributed to near-surface processes or shallow recycling. This helps explain the large spatial and temporal variation of R in regions such as Hawaii, Iceland, Yellowstone, and Ethiopia (59). High Rs are not proof

of a lower mantle origin. Oxygen isotopes also favor a near-surface origin of so-called hotspot signatures (60).

The predictions of recent box models (2–4) regarding the He budget of the Earth are wrong by orders of magnitude (55). The hypothesis that high Rs in basalts and quenched glasses imply “excess” <sup>3</sup>He or a primordial gas-rich reservoir has been falsified.

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