

# **Models for Noble Gases in Mantle Geochemistry: Some Observations and Alternatives**

Anders Meibom<sup>1</sup>, Norman H. Sleep<sup>2</sup>, Kevin Zahnle<sup>3</sup>, Don L. Anderson<sup>4</sup>

<sup>1</sup>Department of Geological and Environmental Sciences,  
320 Lomita Mall, Stanford University, CA 94305, USA

<sup>2</sup>Department of Geophysics, Mitchell Building,  
Stanford University, CA 94305, USA

<sup>3</sup>NASA Ames Research Center, Mail Stop 245-3  
Moffett Field, CA 94035, USA

<sup>4</sup>Seismological Laboratory 252-21,  
California Institute of Technology,  
Pasadena, CA 91125, USA

October 22, 2004.

Geological Society of America Special Paper – in press.

## Abstract

Models for noble gases in the Earth's mantle are evaluated against a number of observational constraints: 1) high  $^3\text{He}/^4\text{He}$  ratios do not correlate with high (initial)  $^3\text{He}$  concentrations, 2) MORB and OIB  $^3\text{He}/^4\text{He}$  data do not represent two different distributions [Anderson 2001], 3) globally robust correlations between  $^3\text{He}/^4\text{He}$  ratios and lithophile isotopic systems are not observed, 4) diverse local correlations exist that are broadly linear, 5) large, local geographical  $^3\text{He}/^4\text{He}$  variations are observed, which are inconsistent with a strongly localized (i.e. plume-stem) flux of high- $^3\text{He}/^4\text{He}$  material, and 6) dramatic temporal  $^3\text{He}/^4\text{He}$  variations are observed on very short time scales ( $10^2$  years). Layered (reservoir) models for noble gases, in which a deep and radially constrained region of the Earth's mantle preserves unradiogenic He and Ne isotopic compositions because of a high noble gas concentration, do not seem consistent with these observations. Heterogeneous (non-layered) mantle models for noble gases, in which the carrier of unradiogenic He is a relatively noble-gas-poor component scattered in the (upper) mantle, appear more consistent with the constraints.

We propose that the carrier of unradiogenic noble gases is primarily olivine. Olivine-rich lithologies, produced in previous partial melting events, are a natural part of the Statistical Upper Mantle Assemblage (SUMA); a highly heterogeneous assemblage of small-to-moderate scale ( $\sim 1$ -100 km) enriched and depleted lithologies with a wide range in chemical composition, fertility, age and isotopic signatures [Meibom and Anderson 2003]. The isotopic signatures of oceanic basalts, including noble gases, are obtained by partial melting of the SUMA under slightly different P-T conditions; i.e. different degrees of partial melting and different degrees of homogenization prior to eruption [Ito and Mahoney 2004; Meibom and Anderson 2003; Morgan and Morgan 1999; Rudge et al. 2004]. Unradiogenic noble gas isotopic compositions are not tracers of deep mantle components in the source materials of oceanic basalts. Noble gas isotopic compositions may, however, indirectly indicate potential temperature, as the order in which different upper mantle lithologies melt depends on the P-T conditions.

## Introduction

Perhaps the most important example of an inferred genetic relationship between a geochemically measurable quantity and a large-scale geophysical phenomenon is the proposed link between mantle plumes and noble gas systematics of oceanic basalts, primarily He. The Classical Model for noble gas systematics in the Earth's mantle holds that the mantle below ~650 km depth represents a largely undegassed reservoir of primordial noble gases. These noble gases are transported to the surface by deep rooted mantle plumes that are associated with intra-plate volcanism, or hot-spots. Through this model, the noble gas systematics of oceanic basalts have become a frequently used, but model dependent, geochemical parameter for discriminating between shallow upper mantle vs. deep lower mantle provenance of their source rocks.

Increasingly, however, geochemists and geophysicists have become uneasy with this classical interpretation of the noble gas geochemistry of mantle-derived rocks. For example, geophysical models of mantle convection find it impossible to keep a large lower-mantle noble-gas reservoir isolated over the time scale of the Earth [Albarède and van der Hilst 2002; Ballentine et al. 2002; Davies 2002; Ferrachat and Richard 2001; Helffrich and Wood 2001; Hunt and Kellogg 2001; Tackley 2000; van Keken and Ballentine 1998, 1999; van Keken et al. 2001, 2002]. Furthermore, tomographic studies are finding a lack of correlation between the imaged depth of inferred mantle plumes and the He isotopic characteristics of the associated hot-spot basalts. Some oceanic islands associated with plumes inferred to originate deep in the mantle are not characterized by 'lower mantle' He isotope compositions (St. Helena and Canary Islands). Other oceanic islands associated with sources that most likely do not originate in the deep mantle (e.g. the Galapagos Archipelago and Iceland) show He isotopic systematics that, within the Classical Model, would be interpreted as signatures of the deep mantle [Foulger and al. 2001; Foulger and Pearson 2001; Montelli et al. 2004]. Although our focus is on oceanic basalts we note that Yellowstone provides another example of a high- $^3\text{He}/^4\text{He}$  hotspot for which seismic evidence suggest an absence of anomalously hot mantle below 200 km [Christiansen et al. 2002].

In this paper we first describe the premises of the Classical Model for noble gas systematics in oceanic basalts. Then we discuss a number of important observations

which seem to require that the Classical Model undergo substantial modification. A number of authors have already, from different vantage-points, explored alternative models (reviewed by Porcelli and Ballentine [2002]). In response to tomographic studies, which were interpreted as evidence for mass transfer through the ~650 km discontinuity [e.g., Albarède and van der Hilst 2002; Grand 1994; van der Hilst et al. 1997], modified versions of the Classical Model have placed the proposed undegassed reservoir at increasingly deeper levels in the mantle. For example, it has been suggested that the undegassed reservoir is confined to the lowermost part of the lower mantle [Kellogg et al. 1999], to the D" layer [DePaolo 2004; Graham et al. 1993; Tolstikhin and Hofmann 2004], or that the outer core may contain substantial amounts of unradiogenic He [Porcelli and Halliday 2001]. Here we refer to these reservoir models collectively as “layered models” for noble gases in mantle geochemistry. We provide a qualitative evaluation of these models, as well as the most recent non-layered models.

The purpose of the present paper is not to present a comprehensive review of the noble gas literature; for in-depth reviews we refer to [Ozima and Podosek 2002; Porcelli et al. 2002]. Nor is the present paper a discussion about the geophysical reality of deep-rooted mantle plumes. The purpose of this contribution is to examine the basis for a set of geochemical models that continues to play a crucial role in the debate about the provenance of mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB). We subsequently discuss properties that would make existing and future models conform better to the currently available data.

### **The Classical Model**

The Classical Model is primarily based on radiogenic and nucleogenic isotopic evolution of He, Ne, and Ar in the mantle, combined with a number of critical observations of the noble gas characteristics of the Earth’s atmosphere, oceanic basalts, and the flow of He and heat out of the mantle [Allègre et al. 1996; Allègre et al. 1986; O’Nions and Oxburgh 1983; Ozima and Podosek 2002]. In the following we briefly describe the fundamental observations that formed the basis for the Classical model.

Helium has two stable isotopes:  $^3\text{He}$  and  $^4\text{He}$ . The former is considered a primordial isotope, because it has not been produced in large quantities since the Big Bang [Ozima and Podosek 2002]. In contrast,  $^4\text{He}$  is constantly produced, primarily in the decay series of U and Th. The  $^3\text{He}/^4\text{He}$  ratio of different components in the Earth's mantle therefore decreases with time. Note that, in contrast with the heavier noble gases, He is continually lost from the top of the atmosphere. The residence time of He in the atmosphere is on the order of  $10^6$  years [Ozima and Podosek 2002] and the present day atmosphere is characterized by a  $^3\text{He}/^4\text{He}$  ratio of  $R_A = 1.39 \times 10^{-6}$  [Ozima and Podosek 2002]. The He isotopic composition of mantle derived basalts is often expressed in units of  $R_A$ . For example, a measured  $^3\text{He}/^4\text{He}$  ratio of  $1.39 \times 10^{-5}$  is reported as  $10R_A$ .

Neon has three stable isotopes:  $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$ . The isotopic composition of Ne changes mainly through the so-called Wetherill reactions:  $^{17}\text{O}(\alpha, n)^{20}\text{Ne}$ ,  $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ ,  $^{24}\text{Mg}(n, \alpha)^{21}\text{Ne}$ , and  $^{19}\text{F}(\alpha, n)^{22}\text{Ne}$  [Ballentine and Burnard 2002; Ozima and Podosek 2002; Porcelli and Wasserburg 1995; Wetherill 1954; Yatsevich and Honda 1997]. Of these reactions, the most important in the Earth's mantle is  $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ , with the energetic  $\alpha$ -particles provided primarily by the decay series of U and Th [Ballentine and Burnard 2002; Graham 2002; Yatsevich and Honda 1997]. For practical purposes, the abundance of  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  can be considered essentially constant through time [Ozima and Podosek 2002]. Some OIB (notably Hawaii and Iceland), some segments of the mid-ocean ridge system, and some plutonic bodies in the continental crust (e.g. the Kola carbonatite-ultramafic complex) are characterized by  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios approaching that of the inferred solar Ne isotopic composition [Dixon et al. 2000; Honda et al. 1993; Moreira et al. 1995; Niedermann et al. 1997; Sarda et al. 2000; Yokochi and Marty 2004]. Note that Trieloff et al. [2000] argue for a meteoritic Ne component in the Earth's mantle.

Argon has three stable isotopes:  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{40}\text{Ar}$ . The two light isotopes are not produced in significant quantities in the mantle whereas  $^{40}\text{Ar}$  is the end product of the branched decay of  $^{40}\text{K}$  [Ozima and Podosek 2002]. The  $^{40}\text{Ar}$  isotope is almost entirely produced in the mantle, with subsequent degassing and accumulative storage in the atmosphere [Allègre et al. 1996; Ozima and Podosek 2002].

The Earth's mantle is continuously degassing, primarily during eruption of oceanic basalts. This degassing has affected the noble gas isotopic composition of both the mantle and the atmosphere. Helium isotopic systematics of oceanic basalts show that MORB is characterized by relatively low and uniform  $^3\text{He}/^4\text{He}$  ratios, usually described as falling within the narrow range from  $7R_A$  to  $9R_A$  [Graham 2002], whereas some OIB are characterized by much higher  $^3\text{He}/^4\text{He}$  ratios and by greater  $^3\text{He}/^4\text{He}$  variability [Graham 2002]. In the Classical Model, the high  $^3\text{He}/^4\text{He}$  ratios in some OIB are interpreted as the result of high concentrations of the primordial isotope  $^3\text{He}$  in the region of the mantle from which these basalts are derived.

The decay series of U and Th produce both  $^4\text{He}$  and heat, in a constant ratio ( $\sim 10^{12}$   $^4\text{He}$  atoms/J) [Ballentine et al. 2002]. However, based on estimates for the Earth's average heat flow and the flux of  $^4\text{He}$  from the mantle, obtained from the time integrated flux of  $^3\text{He}$  into the oceans ( $\sim 1060$  moles/year) and an average  $^3\text{He}/^4\text{He}$  ratio of the upper mantle of  $8R_A$ , it has been estimated that almost one order of magnitude more heat than  $^4\text{He}$  is currently escaping the mantle [O'Nions and Oxburgh 1983; Ozima and Podosek 2002; Porcelli and Ballentine 2002; van Keken et al. 2001]. This has prompted the suggestion that a deep boundary layer exists within Earth's mantle through which heat, but not He, can penetrate [O'Nions and Oxburgh 1983].

Based on assessments of the  $^{40}\text{K}$  budget of the mantle and crust and measurements of the  $^{40}\text{Ar}$  concentration in the atmosphere, it has been estimated that  $\sim 50$ - $70\%$  of the  $^{40}\text{Ar}$  produced in the mantle has been degassed to the Earth's atmosphere [Allègre et al. 1996; Anderson 1989; Porcelli and Ballentine 2002]. This is in rough agreement with estimates of the fraction of the mantle that must have been depleted in incompatible elements in order to account for the formation of continental crust [Anderson 1989; Hofmann 1997]. It is believed that the rest of the  $^{40}\text{Ar}$  is still residing in the mantle, with the implication that either a largely undegassed mantle region exist [Allègre et al. 1986, 1996; Allègre and Turcotte 1985], or degassing of  $^{40}\text{Ar}$  was relatively inefficient [Anderson 1989; Sleep 1979].

In the Classical Model the lower mantle represents a largely undegassed noble gas reservoir dominated by primordial noble gas isotopes, whereas the upper mantle is assumed to be thoroughly degassed and dominated by radiogenic and nucleogenic (in the

case of Ne) isotopes [Allègre 2002; Porcelli and Wasserburg 1995]. Based on estimated parameters, such as the present day lower mantle  $^3\text{He}/^4\text{He}$  ratio (from Hawaiian basalts;  $\sim 30R_A$ ), an initial  $^3\text{He}/^4\text{He}$  ratio of  $\sim 100R_A$ , and lower mantle U and Th concentrations, the concentration of primordial  $^3\text{He}$  in the lower mantle has been calculated to be a factor of  $\sim 220$  times higher than in the degassed upper mantle [Porcelli and Wasserburg 1995; Tolstikhin and Marty 1998]. With the more recent findings of  $^3\text{He}/^4\text{He}$  ratios up to about  $50R_A$  in picritic basalts from Baffin Island [Stuart et al. 2003], this lower mantle/upper mantle  $^3\text{He}$  concentration ratio would increase to  $\sim 340$ . Such numbers have motivated a two-layered convection model for the mantle, with the boundary between the lower and the upper mantle traditionally taken to be at the 670 km seismic discontinuity [Allègre 2002; Allègre et al. 1996]. Here phase transitions (i.e. spinel into perovskite/magnesiowüstite) and/or a chemical barrier have been assumed to keep a lower mantle reservoir isolated. In the Classical Model there is only limited exchange between the upper and lower mantle, except when inferred deep rooted mantle plumes rise from the deep mantle [Kellogg and Wasserburg 1990; Porcelli and Wasserburg 1995] or lower mantle material is entrained in material rising from the inferred boundary at 670 km [Allègre and Turcotte 1985]. A two-layer model has strong implications for mantle dynamics and heat flow [Albarède 1998; Allègre 2002; Ballentine et al. 2002; van Keken et al. 2002]. An alternate layered mantle model has a depleted, degassed and isolated ‘lower mantle’ (Bullen’s Region D) with both OIB and MORB derived from a heterogeneous ‘upper mantle’ [Anderson 1989, 2002].

### **Some observations**

We present a number of observations that appear relevant to the distribution of noble gases in the mantle, which is a key issue in the evaluation of the layered models in general. Subsequently, we discuss alternative, non-layered models for the noble gases that might conform more consistently to these observations, as well as the constraints listed above.

We focus on He isotopic systematics of oceanic basalts because the quality and systematic availability of He isotopic data is superior to that of any other mantle-derived

noble gas. Differences between mantle and atmospheric Ne isotopic compositions and evidence for Xe isotopic fractionation and radiogenic in-growth ( $^{131-136}\text{Xe}$  through fission of  $^{244}\text{Pu}$  ( $T_{1/2} = 80 \text{ My}$ ) and  $^{238}\text{U}$  ( $T_{1/2} = 4.4 \text{ Gy}$ ), and  $^{129}\text{Xe}$  through the  $\beta$ -decay of  $^{129}\text{I}$  ( $T_{1/2} = 16 \text{ My}$ )) offer constraints pertinent to the earliest degassing chronology and noble gas evolution of the atmosphere during a time when the mantle-atmosphere system was strongly affected by the moon-forming impact, the continuous effects of the heavy bombardment, and hydrodynamic escape [Dauphas 2003; Ozima and Podosek 2002; Pepin and Porcelli 2002; Yokochi and Marty 2004; Zahnle et al. 1990]. Our focus here is on evidence pertinent to the distribution of noble gases in the present day mantle. Neon isotopic compositions along the mid-ocean ridge system span about the same range as in OIB [Honda et al. 1993; Moreira et al. 1995, 2001; Niedermann et al. 1997; Trierloff et al. 2000; Yokochi and Marty 2004] with the exception of the extremely non-nucleogenic Ne isotopic compositions reported by Dixon et al. [2000]. The latter data indicate that the Ne isotopic spectrum of oceanic basalts (and its interpretation) is not a fully resolved issue at this point.

#### *Noble gas concentrations in MORB and OIB*

In the layered models, basalts characterized by high  $^3\text{He}/^4\text{He}$  ratios are assumed to have high initial  $^3\text{He}$  concentrations; they tap into the undegassed lower mantle reservoir in which  $^3\text{He}$  concentrations are often assumed to be more than two orders of magnitude higher than in the degassed upper mantle. A reasonable first expectation would therefore be that these basalts would also be characterized by relatively high  $^3\text{He}$  concentrations. This is not observed [Anderson 1998a, 1998b; Farley and Neroda 1998; Ozima and Podosek 2002; Porcelli and Ballentine 2002]. On the contrary, OIB, many of which have high  $^3\text{He}/^4\text{He}$  ratios, are characterized by systematically lower  $^3\text{He}$  concentrations than MORB [Farley and Neroda 1998; Ozima 1994]; indeed there is no example of an OIB in which high  $^3\text{He}/^4\text{He}$  correlates with high  $^3\text{He}$  concentration.

However, degassing clearly plays an important role in the noble gases inventory of any oceanic basalt [Bottinga and Javoy 1990; Hilton et al. 2000; Marty and Zimmermann 1999; Moreira and Sarda 2000; Sarda and Moreira 2002; Yamamoto and Burnard 2004]. The major volatile phases in a basaltic melt are water and  $\text{CO}_2$  [Williams

and Hemley 2001]. During magma ascent, when the lithostatic pressure becomes smaller than the CO<sub>2</sub> saturation pressure, CO<sub>2</sub>-rich bubbles form that scavenge noble gases out of the melt phase according to their solubility in the magma [Hilton et al. 2000; Marty and Zimmermann 1999; Nuccio and Panoita 2000; Yamamoto and Burnard 2004]. The solubility of CO<sub>2</sub> in the magma is an inverse function of the water content [Dixon et al. 1995]. The CO<sub>2</sub> and noble gas concentration in the melt phase, prior to bubble formation, is a function of their solid-melt partitioning coefficients, the degree of fractional crystallization and volatile concentration [Brooker et al. 2003a, 2003b, 2004; Burnard et al. 2002; Marty and Zimmermann 1999; Nuccio and Panoita 2000; Ozima and Podosek 2002].

Many analyzed MORB samples were erupted at water depths greater than 2500 m and the associated pressure reduces the escape of CO<sub>2</sub>-rich bubbles during cooling and solidification. The effect of overlying water pressure is nicely illustrated by Hilton et al. [2000] on a suite of MORB samples from the Reykjanes Ridge, which show a clear correlation between the He concentration and eruption depth (low water contents in the deeply erupted basalts amplify this correlation). Many OIB basalts were erupted at much shallower water depths than the average MORB, or even sub-aerially, which promotes stronger degassing. Different degassing mechanisms or conditions for MORB and OIB have been explored [e.g., Marty and Zimmermann 1999; Moreira and Sarda 2000; Yamamoto and Burnard 2004]. Indeed, degassing might explain most of the observed OIB <sup>3</sup>He deficit compared to MORB values [Farley and Neroda 1998]. However, there is no evidence that, prior to degassing, OIB contained substantially higher concentrations of He (or other noble gases) than MORB, as assumed in the layered models [Yamamoto and Burnard 2004]. Based on a study of degassing of basaltic glasses from the Southwest Indian Ridge and the Amsterdam-St. Paul Plateau, Burnard et al. [2002] concluded that the noble gases were lost from individual magmas, or their source materials, prior to magma mixing. Endmember magmas or source regions with broadly similar He concentrations can explain the general lack of curvature of locally observed mixing lines between He isotopic composition and lithophile tracers (see below), but this requires very specific degassing events. Furthermore, extensive degassing of magmas or their source materials prior to magma mixing is not consistent with the direct transfer of He-rich,

high- $^3\text{He}/^4\text{He}$  lower mantle materials to the shallow upper mantle in plumes, such as it is envisaged in many layered models.

### *The $^3\text{He}/^4\text{He}$ systematics of MORB versus OIB*

One of the major motivations for the layered models is the notion that the He isotopic systematics of MORB and OIB represent two different populations. The MORB reservoir, usually referred to as the ‘convective upper mantle’, is considered to be characterized by a narrow distribution of  $^3\text{He}/^4\text{He}$  ratios, centered around  $8\pm 1R_A$  [Graham 2002]. Analyses of OIB show a much larger spread in  $^3\text{He}/^4\text{He}$  ratios, currently from about  $4R_A$  to  $50R_A$  [Farley and Neroda 1998; Graham 2002; Stuart et al. 2003]. There are, however, two important issues associated with such an interpretation of  $^3\text{He}/^4\text{He}$  ratios in MORB vs. OIB.

First, it is undeniable that the MORB  $^3\text{He}/^4\text{He}$  distribution shows a strong peak around  $8\pm 1R_A$  [Graham 2002]. However, to some degree, the sharpness of this peak is a result of data filtering. The notion that the upper mantle is an extremely homogeneous reservoir has created a precedent for disregarding MORB  $^3\text{He}/^4\text{He}$  ratios that fall outside of the accepted upper mantle range ( $8\pm 1R_A$ ), based on the argument that such discordant He isotopic ratios signal the presence of either deep mantle components (if  $^3\text{He}/^4\text{He} > 9R_A$ ) or crustal components (if  $^3\text{He}/^4\text{He} < 7R_A$ ) mixed into the MORB source region. Decisions to disregard  $^3\text{He}/^4\text{He}$  analyses from the MORB distribution are often, but not always, based on accompanying trace-element or lithophile-element isotopic data in comparison with an inferred (‘canonical’) MORB mantle composition [Meibom and Anderson 2003; Salters and Stracke 2004]. Notwithstanding, the compiled MORB  $^3\text{He}/^4\text{He}$  distributions from the Pacific, Indian and Atlantic oceans show quite extreme outliers. The ranges are  $\sim 6R_A$  to  $\sim 12R_A$  for the Pacific Ocean,  $\sim 6R_A$  to  $\sim 15R_A$  for the Indian Ocean, and  $\sim 6R_A$  to  $\sim 18R_A$  for the Atlantic Ocean [Graham 2002].

Second, although some OIB are characterized by high  $^3\text{He}/^4\text{He}$  ratios it is clear that most show large variations in their He isotopic composition [Farley and Neroda 1998; Graham 2002] and that the OIB  $^3\text{He}/^4\text{He}$  distribution overlaps the MORB distribution. Individual hotspots display  $^3\text{He}/^4\text{He}$  ratios both higher and lower than the typical MORB value; e.g. Azores, Galapagos, Hawaii and Heard Island [Hilton et al.

1995; Kurz et al. 2004; Kurz and Geist 1999; Moreira et al. 1999]. Based on statistical tests, Anderson [2000a; 2000b; 2001] has shown that, at the 95% confidence level, the MORB  $^3\text{He}/^4\text{He}$  distribution is indistinguishable from the OIB distribution. In other words, OIB and MORB  $^3\text{He}/^4\text{He}$  ratios could be part of the same statistical population. This conclusion has been challenged; see discussion in [Graham 2002]. However, we continue to find the approach reasonable and generally accept the conclusion that OIB and MORB do not represent two distinct He isotope distributions.

#### *Correlations between $^3\text{He}/^4\text{He}$ and other isotope systems*

Efforts to identify and characterize a particular mantle component that carries the high  $^3\text{He}/^4\text{He}$  signature have led to the popular view that there is a high  $^3\text{He}/^4\text{He}$  and  $^3\text{He}$  lower mantle reservoir that, in terms of Rb-Sr and Sm-Nd isotope systematics, is moderately depleted and falls between bulk silicate Earth and the so-called Depleted MORB Mantle (DMM) [Ballentine et al. 2002; Farley et al. 1992; Hanan and Graham 1996; Hart et al. 1992; van Keken et al. 2002]. This lower mantle endmember has been named FOZO, PHEM or C. An implication of this approach, in which a variety of other mantle endmembers (EM1, EM2, HIMU, DMM) [Zindler and Hart 1986] form essentially linear mixing trajectories with FOZO, is that the He concentration is broadly similar in all endmembers. This is inconsistent with the layered model assumption of an undegassed reservoir carrying the high- $^3\text{He}/^4\text{He}$  ratios, and requires that the FOZO endmember (or melts derived from it) experienced the right amount of degassing prior to mixing with the other inferred mantle endmembers. Such degassing scenarios represent *ad hoc* adjustments to the layered models and no general degassing mechanism for FOZO-type source material has been suggested.

There are many examples of local correlations between He isotopes, lithophile isotopic systems (i.e. Sm-Nd; U,Th-Pb; Rb-Sr; Lu-Hf; Re-Os) and trace elements in oceanic basalts. However, no globally robust relationships between He isotopes and a non-volatile lithophile trace element or isotopic system have been observed; a positive correlation observed at one locality is matched by a negative correlation in another locality [Blichert-Toft et al. 2003; Eiler et al. 1998; Graham 2002; Graham et al. 1996; Hanan and Graham 1996; Kurz et al. 2004; Kurz and Geist 1999; Stuart et al. 2003;

Valbracht et al. 1996]. Fig. 1 shows three such examples – the correlations between Nd and He isotopes in basalts from Baffin Island, the Galapagos Archipelago, and Samoa [Farley et al. 1992; Kurz and Geist 1999; Stuart et al. 2003]. In the deep core of the Hawaiian Scientific Drilling Project (HSDP) correlations between  $^3\text{He}/^4\text{He}$  and lithophile element isotopic systems appear and disappear at different depths. For example, there is a negative correlation between  $^3\text{He}/^4\text{He}$  and Nd isotope composition in the HSDP core at depths below ~2000 meters below sea level, while a similar correlation cannot be observed in the core above this depth [Kurz et al. 2004]. Often, He isotopic compositions in OIB do not correlate with lithophile element isotopic systems at all [Farley et al. 1993]. This weakens conclusions about the origin of unradiogenic  $^3\text{He}/^4\text{He}$  signatures in oceanic basalts reached on the basis of local trends. Here we discuss briefly two key OIB localities, Hawaii and Iceland (Reykjanes Ridge), where local correlations between  $^3\text{He}/^4\text{He}$  and Pb isotopes recently have been debated [Blichert-Toft et al. 2003; Eiler et al. 1998; Hilton et al. 2000; Kurz et al. 2004]. Correlations between He and Pb isotopes are of special interest because these isotope systems are linked through the decay series of U and Th and because the inferred Th/U elemental ratios could potentially provide some insights into the specific nature of the high  $^3\text{He}/^4\text{He}$  source rock.

Several authors have suggested that a strong positive correlation exist between the  $^3\text{He}/^4\text{He}$  and the  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios in Hawaiian basalts [Eiler et al. 1998; Kurz et al. 2004]. Expressed as  $\Delta^{208}\text{Pb}/^{204}\text{Pb}$  (the deviation from the northern hemisphere reference line [Hart 1984]) vs.  $^3\text{He}/^4\text{He}$ , a positive correlation was observed based on data from shield and pre-shield Mauna Kea and Loihi samples (Fig. 2). High  $^3\text{He}/^4\text{He}$  ratios were found to be associated with thorogenic Pb, which prompted the proposal that the mantle source of the high  $^3\text{He}/^4\text{He}$  ratios has undergone closed system evolution with high Th/U ratios [Eiler et al. 1998; Kurz et al. 2004]. However, the original, well-defined correlation partly deteriorates when additional data, notably from Mauna Loa, are included (Fig. 2). Furthermore, Blichert-Toft et al. [2003] observed an even stronger positive correlation between  $^3\text{He}/^4\text{He}$  and  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  (the radiogenic in-growth ratio from the decays of  $^{232}\text{Th}$  ( $^{208}\text{Pb}^*$ ) and  $^{238}\text{U}$  ( $^{206}\text{Pb}^*$ ), respectively) in Mauna Kea samples from the HSDP core. Blichert-Toft et al. [2003] showed that such a positive correlation cannot be explained solely by variations in the Th/U ratio of the source rock. In fact, radiogenic in-

growth in a closed system with a broadly uniform  $^{238}\text{U}/^3\text{He}$  ratio but variable Th/U would produce a negative correlation between  $^3\text{He}/^4\text{He}$  and  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ , opposite to what is observed [Blichert-Toft et al. 2003]. Thus, at this point, although one might conclude on the basis of Fig. 2 that high  $^3\text{He}/^4\text{He}$  ratios are broadly associated with thorogenic Pb isotope compositions (at least in Mauna Kea and Loihi), there are also strong arguments against a direct coupling between the He isotopic systematics and Pb isotopic systematics [Blichert-Toft et al. 2003; Valbracht et al. 1996].

South of Iceland, on the Reykjanes Ridge, another correlation between He isotopes and uraniumogenic Pb has been reported by Hilton et al. [2000], with direct implications for the layered models (Fig. 3). Hilton et al. [2000] divided the Reykjanes Ridge data into three groups: south of  $58.3^\circ\text{N}$ , between  $58.3^\circ\text{N}$  and  $61.3^\circ\text{N}$ , and north of  $61.3^\circ\text{N}$ . South of  $58.3^\circ\text{N}$  the data show relatively homogeneous  $^3\text{He}/^4\text{He}$  ratios, around 11-12  $R_A$  and fall in a small cluster with low  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios, between 18.1-18.2. Between  $58.3^\circ\text{N}$  and  $61.3^\circ\text{N}$  the data fall on a steeply sloped linear correlation with  $^3\text{He}/^4\text{He}$  in the range from 12-17 $R_A$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios between 18.2-18.3. Magmas from north of  $61.3^\circ\text{N}$  were erupted at relatively shallow depth, have very low He concentrations and were considered to be contaminated by crustal (i.e. radiogenic) He. Hilton et al. [2000] therefore excluded these data from their analyses.

A linear fit can be run through the data points south of  $61.3^\circ\text{N}$  (labeled “a” in Fig. 3). Two end-members were defined in this linear mixing model [Hilton et al. 2000]. One end-member, considered to be the DMM, has  $^3\text{He}/^4\text{He} = 8R_A$  at  $^{206}\text{Pb}/^{204}\text{Pb} = 18.04$ . The other end-member has  $^3\text{He}/^4\text{He} = 33R_A$  at  $^{206}\text{Pb}/^{204}\text{Pb} = 18.7$ . There are two important observations regarding this linear mixing model. **a)** The true high- $^3\text{He}/^4\text{He}$  endmember in Iceland is not at  $33R_A$ , but at least  $43R_A$  [Harlou et al. 2004], and possibly higher [Matsumoto et al. 2002; Stuart et al. 2003]. Extrapolation of the linear fit in Fig. 3 to a radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of 19.3 (close to the maximum measured in Iceland [Breddam et al. 2000]) yields a  $^3\text{He}/^4\text{He}$  endmember value of  $\sim 50$ , which would be enough to account for the  $^3\text{He}/^4\text{He}$  variation currently observed in Iceland [Harlou et al. 2004]. In general, however,  $^3\text{He}/^4\text{He}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  do not correlate on Iceland (Fig. 3) [Breddam et al. 2000]. **b)** A linear fit requires that the He/Pb ratios of the two endmembers are equal. This makes the concentration of He in the high- $^3\text{He}/^4\text{He}$

endmember about one order of magnitude higher than the He concentration of the DMM endmember [Hilton et al. 2000]. As noted before, this He concentration is inconsistent with the undegassed nature of the high- $^3\text{He}/^4\text{He}$  reservoir of the layered models, but similar to the source concentration obtained for a mix between a hypothetical FOZO component and recycled oceanic crust [Ballentine et al. 2002]. However, the same type of mixture (FOZO + recycled slab) does not produce the combination of depleted Nd and Sr isotope compositions and high  $^3\text{He}/^4\text{He}$  ratios that characterize Iceland and the Baffin Island picrites [Stuart and Ellam 2004; Stuart et al. 2003].

In order to accommodate a large difference in He concentration between the low- $^3\text{He}/^4\text{He}$  and the high- $^3\text{He}/^4\text{He}$  endmembers, which would be consistent with the layered models, a non-linear fit to the data was also explored [Hilton et al. 2000]. In this non-linear mixing model (labeled “b” in Fig. 3) the He concentration in the high- $^3\text{He}/^4\text{He}$  endmember is  $\sim 200$  times higher than in the low- $^3\text{He}/^4\text{He}$  endmember, closer to the accepted ratio of the layered models [Porcelli and Wasserburg 1995; Tolstikhin and Marty 1998]. However, this model yields a high- $^3\text{He}/^4\text{He}$  endmember with  $^3\text{He}/^4\text{He}$  around  $18\text{-}19R_A$ , which is insufficient to explain the high  $^3\text{He}/^4\text{He}$  ratios reported in Iceland [Breddam et al. 2000; Harlou et al. 2004]. Furthermore, the non-linear mixing model does not pass through the data points from south of  $58.3^\circ\text{N}$ , which means that this mixing model only fits data in a small range of  $^{206}\text{Pb}/^{204}\text{Pb}$ ; less than 0.1 out of a total  $^{206}\text{Pb}/^{204}\text{Pb}$  range of  $\sim 1.0$  for Iceland [Breddam et al. 2000; Hilton et al. 2000]. Additionally, the non-linear mixing model does not satisfactorily explain the high  $^3\text{He}/^4\text{He}$  ratios of the many data points that fall above this mixing curve (Fig. 3). Hence, a non-linear mixing model, which best represents the basic assumptions of the layered models, does not provide a good solution He and Pb isotope systematics of the Reykjanes Ridge and Iceland.

In summary, the lack of globally robust correlations between He isotopes and non-volatile lithophile elements and their isotopes has made it difficult to establish the geochemical identity of a particular source rock for the high- $^3\text{He}/^4\text{He}$  signatures in oceanic basalts. Furthermore, the local, often linear and opposite correlations that are observed between  $^3\text{He}/^4\text{He}$  and lithophile element isotopic systems (Figs. 1 and 3) are

complicated to interpret within the framework of the layered models because of the requirement that the mixing end-members have broadly similar He concentrations.

#### *Local geographical $^3\text{He}/^4\text{He}$ distributions*

In the layered models, material with high  $^3\text{He}/^4\text{He}$  ratios is transported to the surface from the lower mantle by narrow (diameter < 100 km) plumes. In the popular “concentrically zoned plume” geometry, the high  $^3\text{He}/^4\text{He}$  ratios are often confined to basalts right above the narrow stem of the proposed mantle plume, with increasing amounts of entrained upper mantle material (hence lower  $^3\text{He}/^4\text{He}$  ratios) away from its central axis [e.g., Blichert-Toft et al. 2003; DePaolo et al. 2001; Eisele et al. 2003; Hauri et al. 1994; Kurz et al. 1996, 2004]. However, none of the three highest  $^3\text{He}/^4\text{He}$  localities, for which reasonably systematic He isotope data sets exist (i.e. Iceland, Hawaii and Galapagos) conform to this simple picture.

In Hawaii the He and Nd isotopic distributions have been combined into isotopic maps from which it has been inferred that high  $^3\text{He}/^4\text{He}$  ratios are confined to a narrow plume stem, no more than 50 km in diameter [DePaolo et al. 2001]. On the basis of these observations it was concluded that the assumed lower mantle He is degassed in the earliest stages of melting of the incipient plume material. However, a “narrow plume stem” model is contradicted by the observation of  $^3\text{He}/^4\text{He}$  ratios ranging from  $17R_A$  to  $21R_A$  at South Arch, an off-axis volcanic feature consisting of young (<10 ka), alkalic lava flows located about 200 km to the south and *upstream* of the inferred position of the present day Hawaiian plume [Frey et al. 2000; Hanyu et al. 2004], which is usually placed underneath Loihi [DePaolo et al. 2001]. The alkalic volcanism at South Arch is not directly related to the Hawaiian hot-spot and is most likely a shallow volcanic feature related to plate flexure due to the load of Hawaii on the Pacific plate [Hanyu et al. 2004].

In the Galapagos Archipelago, the island of Fernandina is characterized by the highest  $^3\text{He}/^4\text{He}$  ratios (up to  $\sim 28R_A$ ) and is, based on geochemistry, inferred to lie right above the center of the inferred plume [Graham et al. 1993; Kurz and Geist 1999]. However,  $^3\text{He}/^4\text{He}$  ratios significantly higher than the canonical MORB value (i.e.  $> 9R_A$ ) are found at least 50 km to the north and 100 km to the south of the presumed hotspot track, defining a front of variably high  $^3\text{He}/^4\text{He}$  signatures perpendicular to the motion of

the Nazca plate [Graham et al. 1993; Kurz and Geist 1999]. Age constraints show that the Galapagos volcanoes have been erupting basalts with distinctly different He isotopic compositions, both higher and lower than typical MORB values, simultaneously along this front for at least the last ten thousand years. Local correlations between He isotopes, major elements, trace elements and Nd isotopes (Fig. 1) indicate that this He isotopic variability is not explained by degassing processes, but must be related to source heterogeneity [Kurz and Geist 1999], as it is also the case in e.g. Hawaii [Blichert-Toft et al. 2003; Eiler et al. 1996; Hauri 1996; Kurz et al. 2004; Stolper et al. 2004]. Recent tomographic studies have not detected a deep rooted mantle plume underneath the Galapagos Archipelago [Montelli et al. 2004].

These observations point to a much less confined spatial distribution of the high  $^3\text{He}/^4\text{He}$  ratios than assumed in concentrically zoned plume models, a conclusion that is reinforced at Iceland. Here, the idea of high  $^3\text{He}/^4\text{He}$  ratios associated with early degassed He, narrowly confined to a plume stem, encounters serious difficulties. High  $^3\text{He}/^4\text{He}$  ratios are found much further to the south on the Reykjanes Ridge than any other lithophile trace element or isotopic signature of geochemical “anomaly”. South of 61°N on the Reykjanes Ridge all standard geochemical plume indicators (e.g. La/Sm, as well as Sr, Nd and Pb isotopes) become MORB-like but  $^3\text{He}/^4\text{He}$  ratios remain high; in the range between  $\sim 9R_A$  and  $\sim 18R_A$  [Hilton et al. 2000; Poreda et al. 1986].

Thus, the classical picture of the layered models in which a narrowly confined plume delivers lower mantle material characterized by high  $^3\text{He}/^4\text{He}$  ratios to a well defined melting region in the shallow, homogeneous upper mantle does not appear to be consistent with the many observations of spatially much more widely distributed high  $^3\text{He}/^4\text{He}$  signatures in oceanic basalts.

#### *Temporal $^3\text{He}/^4\text{He}$ variations*

There are few localities where strong age constraints combined with He isotopic data allows time series to be meaningfully developed and evaluated. One exception is the unique record that has become available through the sampling and systematic analysis of the HSDP drill core. Phase 2 of the HSDP sampled the Mauna Kea shield to a depth of more than 3 km represents about 1000 lava flow units and covers a time span of more

than 400,000 years [Blichert-Toft et al. 2003; Kurz et al. 2004; Stolper et al. 2004]. Based on isotopic variations in Pb, Nd, Sr, Hf, major elements (i.e. SiO<sub>2</sub>), and trace elements along the core, it has been shown that the source of the Hawaiian volcanism is geochemically heterogeneous [Blichert-Toft et al. 2003; Eisele et al. 2003; Hauri 1996; Kurz et al. 2004; Stolper et al. 2004]. Analyses of these time series find evidence for fluctuations with a dominant period of ~50 Ka for  $\epsilon_{\text{Hf}}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  [Blichert-Toft et al. 2003] and a dominant period of ~18 Ka for trace elements (e.g. La/Yb, Zr/Nb), Sr isotopes,  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  [Blichert-Toft et al. 2003]. Based on upwelling rates in the range from ~1 cm/year to ~1 m/year, the inferred vertical length scale of this geochemical heterogeneity is estimated to be hundreds of meters to tens of kilometers [Blichert-Toft et al. 2003; Eisele et al. 2003; Kurz et al. 2004]. These length scales are identical to those invoked in the Statistical Upper Mantle Assemblage model [Meibom and Anderson 2003]. Helium isotopes vary significantly along the HSDP core. From a slowly and monotonically increasing baseline ( $^3\text{He}/^4\text{He}$  from 10-15R<sub>A</sub>) there are numerous high- $^3\text{He}/^4\text{He}$  excursions, some reaching up to ~25R<sub>A</sub>. These high  $^3\text{He}/^4\text{He}$  “spikes” are predominantly observed in the older part of the core [Kurz et al. 2004]. In contrast to other isotopic systems, He (and Nd) isotopes do not seem to have a periodic component [Blichert-Toft et al. 2003]. In other words, high  $^3\text{He}/^4\text{He}$  excursions seem to be a stochastic signal, randomly over-printing the moderately high and still quite variable  $^3\text{He}/^4\text{He}$  baseline [Blichert-Toft et al. 2003; Kurz et al. 2004].

The average duration of the high- $^3\text{He}/^4\text{He}$  excursions in the HSDP Mauna Kea core is estimated to be 15(±9) Ka (n=6), but in some cases these excursions are defined by single lava flows indicating that fluctuations in the  $^3\text{He}/^4\text{He}$  ratio of the erupted basalts can take place on much shorter time scales [Kurz et al. 2004]. This is supported by data from a stratigraphically and paleomagnetically controlled drill core of shield-stage lavas from Kauai [Mukhopadhyay et al. 2003]. In the Kauai shield-stage lavas the  $^3\text{He}/^4\text{He}$  ratios are generally much higher than in Mauna Kea or Mauna Loa; within the range from 17R<sub>A</sub> to 28R<sub>A</sub>. However, as in the HSDP core, the  $^3\text{He}/^4\text{He}$  are found to vary erratically, with large jumps from ~19R<sub>A</sub> to ~27R<sub>A</sub> occurring on time scales as short as 100 years [Mukhopadhyay et al. 2003]. Note that, at Réunion Island moderately unradiogenic

$^3\text{He}/^4\text{He}$  ratios have been erupted without substantial variability ( $12.5\text{-}13.5R_A$ ) for a time period of  $\sim 360,000$  years [Graham et al. 1990].

As discussed by Mukhopadhyay et al. [2003], the observed rapid, geochemical variations in Hawaii indicate that distinct mantle components or lithologies were sampled and that geochemical signatures were poorly homogenized prior to eruption [Meibom and Anderson 2003; Mukhopadhyay et al. 2003]. In Kauai, He isotopic variations correlated with Sr and Nd (most evident in West Kauai), in combination with inferred major element variability [Mukhopadhyay et al. 2003], support the general notion that the source of Hawaiian volcanism is characterized by relatively coarse geochemical heterogeneity on characteristic length scales of one to tens of kilometers [Blichert-Toft et al. 2003; Eiler et al. 1996; Hauri 1996; Kurz et al. 2004; Meibom and Anderson 2003; Mukhopadhyay et al. 2003; Stolper et al. 2004]. Rapidly varying  $^3\text{He}/^4\text{He}$  ratios in Hawaiian basalts (indeed in any basalt) indicate that the source component carrying the high  $^3\text{He}/^4\text{He}$  signal is volumetrically minor. High  $^3\text{He}/^4\text{He}$  ratios are only observed when this component is present in the melting zone and when contributions from the different lithologies in the source are not thoroughly homogenized [Mukhopadhyay et al. 2003].

As an aside, Mukhopadhyay et al. [2003] observed that the very high  $^3\text{He}/^4\text{He}$  ratios ( $17\text{-}28R_A$ ) captured in Kauai during the shield stage breaks with the notion that such high  $^3\text{He}/^4\text{He}$  ratios are restricted to the pre-shield stage. Furthermore, the occurrence of high  $^3\text{He}/^4\text{He}$  ratios in young alkalic lava flows at South Arch ( $17R_A$  to  $21R_A$ ) [Frey et al. 2000; Hanyu et al. 2004], in alkalic flow units from e.g. the Galapagos Archipelago [Kurz and Geist 1999] and the Juan Fernandez Archipelago [Farley et al. 1993] cautions that *a priori* filtering of He isotopic data on the basis of a temporal criteria such as “post-shield” or a chemical criteria such as alkalinity might not be universally warranted.

## **Discussion**

The observations described above draw a picture of the He isotopic distribution in the mantle quite different from that of the layered models. As has been noted previously [e.g., Anderson 1998a; Farley and Neroda 1998; Porcelli and Ballentine 2002], there is

no evidence that the source of the high- $^3\text{He}/^4\text{He}$  ratios is also characterized by high  $^3\text{He}$  concentrations. Furthermore, the distribution of the high- $^3\text{He}/^4\text{He}$  carrier is generally not confined to the melting zones of inferred plume stems [Frey et al. 2000; Hanyu et al. 2004; Hilton et al. 2000; Poreda et al. 1986]. In combination with the observed rapid, stochastic  $^3\text{He}/^4\text{He}$  fluctuations [e.g., Blichert-Toft et al. 2003; Mukhopadhyay et al. 2003], which suggest that the carrier of the high- $^3\text{He}/^4\text{He}$  is a volumetrically minor component only detectable when the mantle components in the source are poorly homogenized [Mukhopadhyay et al. 2003], this could indicate that the high- $^3\text{He}/^4\text{He}$  carrier is a more widespread component in the upper mantle. The absence of a correlation between  $^3\text{He}/^4\text{He}$  signatures in OIB and tomographically inferred depths of plume stems strongly indicate that high- $^3\text{He}/^4\text{He}$  ratios are not confined to the lower mantle [Christiansen et al. 2002; Foulger and al. 2001; Foulger and Pearson 2001; Montelli et al. 2004]. The lack of consistent correlations between He isotopes and lithophile isotopic systems or trace elements suggest that the carrier phase of the high- $^3\text{He}/^4\text{He}$  ratios is a geochemically neutral phase and that the observed contradictory correlations are controlled by the other components in the source assemblage, independent of the presence or absence of the high- $^3\text{He}/^4\text{He}$  ratios.

How do we reconcile these observations with other constraints listed above, such as the heat flow, the  $^{40}\text{Ar}$  budget of the Earth's mantle and Ne isotopic systematics? At the moment it is clear that no single model fully satisfies all geochemical and geophysical constraints [Porcelli and Ballentine 2002].

#### *Distribution of the high- $^3\text{He}/^4\text{He}$ carrier - the Statistical Upper Mantle Assemblage*

There seems little doubt that the best estimate of the  $^3\text{He}/^4\text{He}$  ratio for the upper mantle is the MORB value of 8-9 $R_A$  [Graham 2002]. The more important questions concern how the unradiogenic He isotopic compositions are distributed and why high  $^3\text{He}/^4\text{He}$  ratios are not, in general, observed along the mid-ocean ridge system?

Evidence is strong for geochemical source heterogeneity in most well studied high- $^3\text{He}/^4\text{He}$  localities; e.g. Hawaii, Iceland, Galapagos, Samoa [Blichert-Toft et al. 2003; Breddam 2002; Breddam et al. 2000; Eiler et al. 1996; Farley et al. 1992; Kurz et al. 2004; Kurz and Geist 1999; Mukhopadhyay et al. 2003; Stolper et al. 2004]. In

general, indications of the presence of recycled crustal materials in the upper mantle are ubiquitous in mantle derived materials [e.g., Eiler et al. 1999; Hofmann 1997; Meibom and Anderson 2003; Meibom et al. 2002; Zindler and Hart 1986]. Where available data have allowed the characteristic length scales of this geochemical heterogeneity to be determined, the resulting estimates fall within the range from hundreds of meters to tens of kilometers [e.g., Batiza 1984; Blichert-Toft et al. 2003; Fornari et al. 1985; Helffrich and Wood 2001; Kellogg et al. 2002; Kurz et al. 2004; Kurz and Geist 1999; Lassiter et al. 2003; Meibom et al. 2002; Reisberg and Zindler 1986; Woodhead and McCulloch 1989; Zindler and Hart 1986; Zindler et al. 1984]. Those are the length scales characterizing the dimensions of subducting slabs, their sub-units and residues, respectively. Others have looked at longer wavelength variation along ridges and determined characteristic lengths between ~150 and 400 km [Butler et al. 1993; Graham et al. 2001]. Partial melting underneath mid-ocean ridges and large igneous provinces, creation of variably depleted residues, extraction of basalts, and subsequent subduction of oceanic crust with associated sediments and thermal lithosphere are probably the most important processes by which geochemical heterogeneity is continuously supplied to the upper mantle [Albarède and van der Hilst 2002]. Other important contributors include sub-continental lithosphere, metasomatic reactions and continental crust [Hofmann 1997; Workman et al. 2004]. Subducted and recycled components are dispersed in the upper mantle by convection and juxtaposed with depleted residues. The result is a highly heterogeneous assemblage of small-to-moderate scale (~1-100 km) enriched and depleted lithologies with a wide range in chemical composition, fertility, age, and isotopic signatures. This configuration has been called the Statistical Upper Mantle Assemblage (SUMA) [Meibom and Anderson 2003]. Locally, the exact nature of the SUMA depends on the combined effects of prior melt extraction, subduction processes, and mantle motions.

Note that the coarse length scale of the SUMA model is an essential feature that distinguishes this model from e.g. the Marble Cake model, in which sub-meter-sized veins of pyroxenite are distributed in a matrix of depleted residue [Fitton and Dunlop 1985]. The more fine-scaled structure of the Marble Cake model is the proposed outcome of efficient convective stirring and mixing of depleted residues and recycled components

in the upper mantle [Allègre and Turcotte 1986; Coltice and Richard 2002; Fitton and Dunlop 1985; Kellogg et al. 2002]. However, Kogiso et al. [2004] have shown that such a fine-scaled distribution of enriched materials does not allow the extraction of geochemically enriched basalts, because even early partial melts (primarily vein material) equilibrate with the host rock (depleted residue) prior to extraction. The analysis of Kogiso et al. [2004] combined with observations of ubiquitous geochemical variation in oceanic basalts therefore imply that the primary process responsible for the destruction of geochemical heterogeneity in the upper mantle is partial melting of a relatively coarse assemblage of different lithologies, such as is invoked in the SUMA model.

Partial melting and mixing of melts prior to eruption will tend to average out extreme compositions and the extracted magmas are to be considered averages of underlying source heterogeneity. The Central Limit Theorem predicts that any distribution of averages will approach a Gaussian distribution [Bracewell 2000; Meibom and Anderson 2003]. Thus, a key prediction of the SUMA model is that geochemical data derived from oceanic basalts will tend to form distributions that *approach* Gaussian shapes. This is observed for a number of large Pb, Sr, and Nd isotopic data sets, including examples of MORB (East Pacific Rise, Mid-Atlantic Ridge, and Southwest Indian Ridge) and OIB (Hawaii and Iceland) [Ito and Mahoney 2004; Kellogg et al. 2002; Meibom and Anderson 2003; Rudge et al. 2004], as well the MORB He isotopic dataset [Anderson 2000a; Meibom et al. 2003]. Indeed, it is becoming increasingly clear that the vast majority of the observed MORB and OIB isotopic and trace element compositions can be explained by partial melting of essentially the same underlying SUMA, by allowing for reasonable differences in the degree of homogenization and in melting regime (i.e. P-T conditions) between MORB and OIB [Ito and Mahoney 2004; Meibom and Anderson 2003; Morgan 2001; Morgan and Morgan 1999; Rudge et al. 2004]. The SUMA idea thus breaks with the traditional concepts of ‘geochemical reservoirs’ or ‘endmembers’ and replaces them with statistical distributions of lithologic components and sampling theory.

We propose that the carrier of the high- $^3\text{He}/^4\text{He}$  ratios is part of the SUMA. Accordingly, the apparent homogeneity of MORB, with a well defined mode around 8-9 $R_A$ , represents a fairly good estimate of the upper mantle with more extreme outliers effectively averaged out in the partial melting and magma mixing processes under the

mid-ocean ridge system [e.g., Anderson 2000b; Meibom et al. 2003]. More extreme, unradiogenic (as well as radiogenic)  $^3\text{He}/^4\text{He}$  compositions will only be observed when *a*) these components are locally present, and *b*) when melts from the different lithologies in the SUMA are poorly homogenized prior to extraction of the basalt [Anderson 2000a, 2000b, 2001; Coltice and Richard 2002; Meibom et al. 2003; Mukhopadhyay et al. 2003]. A widespread distribution of high- $^3\text{He}/^4\text{He}$  ratios in the upper mantle appears to be more consistent with the observations discussed above, which indicate that high- $^3\text{He}/^4\text{He}$  ratios are not confined to narrow melting zones associated with OIB volcanism [e.g., Anderson 2000a, 2000b, 2001; Frey et al. 2000; Hanyu et al. 2004; Hilton et al. 2000; Kurz and Geist 1999; Poreda et al. 1986]. Such a spatial distribution of high- $^3\text{He}/^4\text{He}$  material scattered throughout the (upper) mantle is generally consistent with the most recent modeling efforts of Xie and Tackley [2004], van Keken et al. [2001], van Keken and Ballentine [1999], Ballentine et al. [2002] and Albarède [2004]. These mantle models produce a scattered distribution of high  $^3\text{He}/^4\text{He}$  material, either in the form of remnant, undegassed primordial material or as ancient depleted residues that, depending on the relatively compatibility of U, Th and He, can preserve unradiogenic  $^3\text{He}/^4\text{He}$  as high as  $\sim 75R_A$  in the present day mantle; e.g. [Xie and Tackley 2004]. Within the context of these modeling efforts, the exact nature of the high- $^3\text{He}/^4\text{He}$  carrier phase becomes a critical issue: is it preferentially primordial, un-degassed material rich in noble gases, or is it depleted residue from which more U+Th has been extracted than He?

#### *Carrier of the high $^3\text{He}/^4\text{He}$ signal*

Preservation of unradiogenic He and Ne isotopic compositions in the Earth's mantle requires that He/(U+Th) and Ne/(U+Th) ratios be high, so that the production of  $\alpha$ -particles from the decay series of U and Th have only minor impact on the isotopic composition of He (through direct addition of  $^4\text{He}$ ) and Ne (through the  $^{18}\text{O}(\alpha,n)^{21}\text{Ne}$  Wetherill reaction), respectively. There are only two ways to obtain this. Either the concentrations of He and Ne are very high, or the concentrations of U and Th are very low. The layered models assume the first option. However, as we have discussed above, and as pointed out by many other authors: even taking into account different degrees of degassing of MORB and OIB, there is no evidence that unradiogenic He and Ne isotope

compositions correlate with relatively high initial He and Ne concentrations. The observed linear mixing trends between  $^3\text{He}/^4\text{He}$  and lithophile element isotopic systems (Fig. 1) demand broadly similar concentrations of noble gases in the different source materials that undergo partial melting [e.g., Graham 2002; Hilton et al. 2000; Porcelli and Ballentine 2002]. Thus, available data force an important modification to be made to the layered models: the carrier material of the unradiogenic He and Ne isotopes must undergo degassing prior to mixing with the already degassed upper mantle. Importantly, such a special degassing process is required independently of how the primordial noble gas-rich source material is distributed; i.e. whether this material is confined to the lower mantle or is dispersed as surviving, undegassed blobs throughout the mantle [Albarède 2004; Becker et al. 1999; Morgan and Morgan 1999; Porcelli and Ballentine 2002; Xie and Tackley 2004]. At this stage, such a degassing step is purely speculative.

For these reasons, we favor a carrier phase for the unradiogenic He and Ne isotopic compositions that is characterized by moderately low noble gas concentrations, but very low U and Th concentrations [Coltice and Richard 2002]. The existence and nature of a phase or lithology with these properties depends on the relative compatibilities of He+Ne and U+Th, which are poorly constrained [Graham et al. 1990; Graham 2002; Ozima and Podosek 2002], and their relative solubilities in magmas. Nevertheless, the most recent experimental work indicates that the ubiquitous mantle mineral olivine might be a good candidate. Brooker et al. [2003b] have determined the olivine/melt partitioning of He, U and Th and report that, for fairly high degrees of melting and in the absence of a gas phase (i.e.  $\text{CO}_2$  bubbles), a small but significant amount of He is retained in the olivine crystal lattice (i.e. He is found to be moderately incompatible) whereas U and Th are several orders of magnitude more incompatible and extremely depleted in the olivine crystals. If these results are robust, they provide the first direct experimental evidence that partial melting events in the upper mantle, which precipitate olivine, might produce highly depleted harzburgitic or dunitic lithologies that can retain low concentration of He (and Ne) but essentially no U or Th [Anderson 1998a; Coltice and Ricard 1999; Coltice and Richard 2002; Graham et al. 1990; Xie and Tackley 2004]. Another plausible mechanism is capture by overgrowth of noble gas-rich  $\text{CO}_2$  bubbles in olivine crystals. This is observed to occur under relatively shallow mantle

conditions (<50 km), where magmas can become saturated in CO<sub>2</sub> [Bottinga and Javoy 1990; Kaneoka and Takaoka 1978; Natland 2003] and offers another mechanism by which olivine precipitating from a magma can effectively separate He+Ne from U+Th [Natland 2003]. Thus, olivine-rich lithologies could have the capability to retain unradiogenic noble gas isotopic compositions; i.e. act as noble gas ‘time capsules’, as observed in the 380 My old dunites and pyroxenites from the Kola carbonatite-ultramafic complex, Eastern Baltic Shield, Russia [Yokochi and Marty 2004]. Importantly, such olivine-rich lithologies are a natural part of the SUMA [Meibom and Anderson 2003].

A particularly appealing aspect of a SUMA model in which olivine-rich lithologies are the carriers of unradiogenic noble gas signatures is that olivine is a geochemically “neutral” mineral. The olivine crystal not only rejects U and Th, but also e.g. Sm, Nd, Rb, Sr, Lu, Hf, and other trace elements. Thus, the participation of olivine-rich lithologies in partial melting processes does not affect the isotopic, nor the trace element signatures of the resulting magma. Correlations between He isotopes and other isotopic systems will therefore be unrelated to the high-<sup>3</sup>He/<sup>4</sup>He carrier. The observed linear and contradictory correlations (e.g. Fig. 1) between <sup>3</sup>He/<sup>4</sup>He and other lithophile isotopic systems are expected within the framework of the SUMA model because these correlations are controlled primarily by other components in the source assemblage, not by the high-<sup>3</sup>He/<sup>4</sup>He component. In other words, ancient olivine-rich lithologies, the residues of former partial melting and degassing events, can deliver unradiogenic He and Ne isotopic compositions without becoming an effective mixing component for other isotopic systems, with the potential exception of Os isotopes [Schaefer et al. 2002] and transition metals (i.e. Mn, Fe, Ni, Co) [Lee 2004].

Olivine precipitated from open system magmas will capture noble gas abundances with a clear imprint of degassing; i.e. solubility controlled elemental fractionation. Remelting of such material in later partial melting events provides an explanation for the intriguing <sup>4</sup>He/<sup>40</sup>Ar\* source heterogeneity and the correlation between initial <sup>4</sup>He/<sup>40</sup>Ar\* and <sup>3</sup>He/<sup>4</sup>He observed in MORB from the Southeast Indian Ridge, which otherwise appear enigmatic [Burnard et al. 2004]. Furthermore, melting and release of unradiogenic <sup>3</sup>He/<sup>4</sup>He from a distribution of ancient olivine-rich lithologies as part of the SUMA

configuration provides a logical explanation for the observed, stochastic and rapid temporal  $^3\text{He}/^4\text{He}$  fluctuations discussed above.

*Different noble gas models – encompassing other constraints*

Based on the inferred distribution of unradiogenic He and Ne in the mantle, alternatives to the Classical Model for noble gases in the mantle (described in the introduction) can be divided into two basic categories: layered-mantle and non-layered-mantle noble gas models. We consider layered mantle models to include scenarios in which a deep and radially constrained region of the Earth, such as the outer core [Porcelli and Halliday 2001], the D" layer [Tolstikhin and Hofmann 2004], or lowermost part of the mantle [Kellogg et al. 1999] is stable against convection over the age of the Earth and preserves unradiogenic He and Ne isotopic compositions because of a high initial concentration of primordial noble gas isotopes. Non-layered models for the noble gases include those in which the unradiogenic He and Ne compositions are not constrained to a specified deep layer or region in the mantle, but are scattered throughout the mantle (or the upper mantle), as a result of convective motions. Non-layered models can therefore invoke whole mantle convection [Albarède 1998, 2004; Ballentine et al. 2002; Coltice and Ricard 1999, 2002; Morgan and Morgan 1999; van Keken and Ballentine 1998, 1999; Tackley 2000; van Keken et al. 2001; Xie and Tackley 2004], but this is not always the case [Anderson 2002].

A successful model must also be able to conform to the constraints offered by the  $^{40}\text{Ar}$  inventory of the atmosphere and the apparent imbalance between the flux of heat and He from the mantle. The  $^{40}\text{Ar}$  constraint is that an estimated ~50% of the mantle-produced  $^{40}\text{Ar}$  has been degassed and is now residing in the atmosphere; the rest remains in the mantle [Allègre et al. 1996]. The He- and heat-flux imbalance is that significantly less  $^4\text{He}$  is degassing from the mantle than is predicted from the inferred radiogenic element budget and the observed heat flow [Ballentine et al. 2002; O'Nions and Oxburgh 1983; Ozima and Podosek 2002; Tackley 2000; van Keken et al. 2001].

Layered mantle models for the noble gases generally embrace the  $^{40}\text{Ar}$  constraint by inferring the existence of an undegassed (i.e noble gas-rich) reservoir in the deep Earth, and meet the He/heat flux ratio constraint with the hypothesis that a boundary

layer separates this reservoir from the mantle above it and that this boundary layer preferentially allows heat to penetrate while He is more effectively retained [Kellogg et al. 1999; O'Nions and Oxburgh 1983; Tolstikhin and Hofmann 2004]. The existence of such a boundary layer is hard to prove and it has therefore remained a hypothesis in layered mantle models.

Non-layered models find that ~50% of the produced  $^{40}\text{Ar}$  is retained in the mantle during its 4.5 Gy of evolution; mainly because strong degassing occurs early in the evolution of the mantle when limited  $^{40}\text{Ar}$  had been produced [Ballentine et al. 2002; Coltice and Ricard 1999, 2002; Sleep 1979; van Keken and Ballentine 1998, 1999; van Keken et al. 2001; Xie and Tackley 2004]. Thus, non-layered models encounter no problems in meeting the  $^{40}\text{Ar}$  constraint without the need to invoke an undegassed reservoir in the deeper part of the Earth. However, at this point it is not clear if non-layered models can also be developed to meet the He/heat flux constraint [Ballentine et al. 2002; van Keken et al. 2001]. The processes by which noble gasses are extracted from the mantle are clearly complex and involve poorly constrained parameters, such as the crystal-melt and melt-gas partitioning coefficients, effects of magma composition, pressure and temperature [Ozima and Podosek 2002]. It is unknown to what degree the degassing processes allow separation of He and heat. Furthermore, noble gases are lost from the mantle primarily along the mid-ocean ridge system, i.e. from a localized zone that exhibits great spatial and temporal variability in eruption rate [Schlosser and Winckler 2002]. In contrast, heat is lost more uniformly across the mantle-crust boundary. Thus, there appear to be many reasons why heat and He would be lost from the mantle at different rates at any given moment. These simple facts could lead to the discrepancy between observed and predicted He/heat flux ratio [O'Nions and Oxburgh 1983]. Indeed, van Keken et al. [2001] found that the different dynamic time scales of heat and He extraction from the mantle allow for dramatic temporal variations in the He/heat flux ratio, and found that some of these variations brought the He/heat flux ratio down to the currently observed level. However, large excursions from the predicted He/heat flux ratio were found to be of short duration (compared to the geological time scale) and although it was concluded that the results allow for the hypothesis that we live in “special times”, such an hypothesis was considered quite unlikely on statistical

grounds. Introducing a higher level of complexity to the degassing process would be a valuable next step in these important modeling efforts.

Ballentine et al. [2002] have pointed out that the estimated flux of  $^4\text{He}$  from the mantle, which is obtained from the time integrated flux of  $^3\text{He}$  into the oceans and the inferred  $^3\text{He}/^4\text{He}$  ratio of the upper mantle of  $\sim 8R_A$ , is only representative of the last 1000 years; the stirring time scale of the deep oceans. This leaves the distinct possibility that the He concentration of the upper mantle might not be estimated precisely. Ballentine et al. [2002] argued that increasing the estimated  $^3\text{He}$  concentration of the upper mantle by a factor of 3.5 removes the requirement for a deep mantle reservoir. This was termed the “zero paradox  $^3\text{He}$  concentration”. In this “zero paradox” model, the imbalance between the heat and He fluxes was explained by short time scale variations in combination with large scale dynamic variance created by mantle convection [van Keken et al. 2001]. The efficiency with which magmas can be brought to the surface vs. the rate at which their contained gases are brought to the surface is an important issue. If magmas degas at some depth and volatiles are trapped, e.g. as  $\text{CO}_2$ -rich bubbles in olivine [Natland 2003] or in residue fractures/cavities [Anderson 1998b], then the gas content of erupted magmas is not necessarily the same as in the source region or the upwelling magma.

## **Conclusions and outlook**

In line with a number of previous authors we conclude that noble gas systematics of oceanic basalts do not require the kind of mantle layering envisaged in the layered models or the existence of a large scale primordial reservoir in the deep Earth [e.g., Albarède and van der Hilst 2002; Anderson 1998a, 2002; Ballentine et al. 2002; Morgan and Morgan 1999; van Keken et al. 2001; Xie and Tackley 2004]. The kind of layering discussed by Anderson [2002], which has a depleted, degassed and inaccessible residual deep mantle is not ruled out by these considerations. In this model, which is based on mass balance considerations, all of the important geochemical tracers, including noble gases, are in the crust and upper mantle and the buoyancy of olivine and olivine-rich lithologies suggests that the main source of helium may be in the shallow mantle.

Non-layered mantle models can account for the  $^{40}\text{Ar}$  budget and preservation of high- $^3\text{He}/^4\text{He}$  material scattered in the mantle, either as relatively undegassed blobs [e.g., van Keken et al. 2001; Xie and Tackley 2004] or as ancient residues from partial events moderately depleted in noble gases, but extremely depleted in U+Th [Anderson 1998a; Brooker et al. 2003b, 2004; Coltice and Richard 2002; Graham et al. 1990; Xie and Tackley 2004].

A number of observations are of importance in assessing the distribution of noble gases in the mantle, including 1) lack of evidence for high  $^3\text{He}/^4\text{He}$  ratios correlating with high initial He concentrations, 2) the MORB and OIB  $^3\text{He}/^4\text{He}$  distributions are most likely identical, 3) globally robust correlations between  $^3\text{He}/^4\text{He}$  ratios and lithophile isotopic systems are not observed, 4) the correlations we do observe are diverse and broadly linear, 5) large, local geographical  $^3\text{He}/^4\text{He}$  variations are observed, which are inconsistent with a strongly localized (i.e. plume-stem) delivery of high- $^3\text{He}/^4\text{He}$  material, and 6) dramatic temporal  $^3\text{He}/^4\text{He}$  variations are observed on very short time scales. Based on this collected set of observations we favor a non-layered mantle model for the noble gases in which the carrier of unradiogenic noble gases is a relatively gas-poor phase spatially scattered in the mantle. The unradiogenic noble gas carrier could be part of the Statistical Upper Mantle Assemblage (SUMA), a highly heterogeneous assemblage of small-to-moderate scale (~1-100 km) enriched and depleted lithologies with a wide range in chemical composition, fertility, age, and isotopic signatures [Meibom and Anderson 2003]. The isotopic signatures of oceanic basalts (MORB and OIB) are obtained by different degrees of partial melting (i.e. different P-T conditions) of the SUMA and different degrees of homogenization prior to eruption [Ito and Mahoney 2004; Kellogg et al. 2002; Meibom and Anderson 2003; Morgan and Morgan 1999; Rudge et al. 2004].

Based on the most recent experimental and observational work on olivine [Brooker et al. 2003b, 2004; Natland 2003], we currently favor this mineral as the main carrier of unradiogenic noble gas isotopic compositions. Olivine-rich lithologies, which are a natural part of the SUMA, have the capability to retain unradiogenic He and Ne isotopic isotope compositions [Yokochi and Marty 2004]; i.e. act as noble gas ‘time capsules’. Furthermore, olivine is a geochemically “neutral” mineral that not only rejects

U and Th, but also other trace elements. Ancient olivine-rich lithologies, the residues of former partial melting events, can deliver unradiogenic He and Ne isotopic compositions without becoming an effective mixing “endmember” for other isotopic systems (i.e. Nd, Sr, Pb). Correlations between He isotopes and other isotopic systems will therefore be unrelated to the high- $^3\text{He}/^4\text{He}$  carrier because other components in the SUMA control these correlations. Furthermore, melting and release of unradiogenic  $^3\text{He}/^4\text{He}$  from a distribution of ancient olivine-rich lithologies as part of the SUMA configuration provides an mechanism for the stochastic and rapid temporal  $^3\text{He}/^4\text{He}$  fluctuations that are observed in Hawaii and elsewhere.

An important corollary of these conclusions is that noble gas isotopic signatures cannot be applied as geochemical indicators of the involvement of deep mantle material in the source for oceanic basalts. However, because different lithologies melt under different P-T conditions it is possible that noble gas isotopic systematics of oceanic basalts in some cases indirectly indicate the potential temperature in the upper mantle region undergoing partial melting. This possibility deserves more consideration.

As we move forward towards a better understanding of the geochemical behavior of the noble gases, several issues appear particularly important to address in future experimental and modeling efforts. These include an improved knowledge about the partitioning behavior of noble gases between melt and the different dominant mantle minerals, notably olivine and pyroxene [Brooker et al. 2003b, 2004]. Such data are pivotal, not only to the mechanism(s) for preserving unradiogenic noble gas compositions in different lithologies in the mantle, but also to an improved understanding of the dynamic decoupling of He and heat fluxes from the mantle. It may be, of course, that the separation of U+Th from He+Ne primarily depends on partitioning between melt and gas, and not between melt and solid. From a modeling perspective, it would be very useful to assess how well whole mantle convection models perform with respect to the preservation of unradiogenic Ne isotopic compositions.

## **Acknowledgements**

This work was supported in part by NSF grant EAR-0309414 and by the NASA Planetary Atmospheres Program. A. M. is grateful for inspiring discussions with Jim Natland, Pete Burnard, Francis Albarède, Don DePaolo and his students, Tom Sisson, John Eiler, Alan Brandon, Garrett Ito and Cin-Ty Lee. Don DePaolo is thanked for sharing his compiled data base from the HSDP. Constructive and thorough reviews were provided by Dave Graham, Chris Ballentine, Paul Tackey, and Editor Gillian Foulger. Their efforts are greatly appreciated.

**Figure 1.**  $^3\text{He}/^4\text{He}$  plotted against  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios for picritic basalts from Baffin Island [Stuart et al. 2003], tholeiitic to alkalic basalts on the Galapagos Islands [Kurz and Geist 1999], and alkalic basalts to hawaiites on Samoa [Farley et al. 1992]. With the exception of one outlier, the Baffin Island picrites define a strong positive correlation. The Samoa data also define a positive correlation, sub-parallel to the Baffin Island trend, but displaced significantly from it. Galapagos basalts define a weaker, but negative correlation.

**Figure 2.**  $^3\text{He}/^4\text{He}$  plotted against  $\Delta^{208}\text{Pb}/^{204}\text{Pb}$ . Data from Hawaii, the Galapagos Archipelago and Samoa [Eiler et al. 1998; Farley et al. 1992; Kurz and Geist 1999; Mukhopadhyay et al. 2003]. Mauna Kea data from the HSDP compiled by Don DePaolo (personal communication, 2004).  $\Delta^{208}\text{Pb}/^{204}\text{Pb}$  is the vertical deviation in  $^{208}\text{Pb}/^{204}\text{Pb}$  from the Northern Hemisphere Reference Line in a plot of  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{208}\text{Pb}/^{204}\text{Pb}$  [Hart 1984]. In Hawaii, the data from Mauna Kea, Loihi and Kauai collectively define a broad, positive correlation (mainly created by the Mauna Kea HSDP data). However, Mauna Loa data do not fall on this positive trend. The data from the Galapagos Islands show no clear relationship between He and Pb isotopes. Samoa data show a negative (but weaker) correlation. Neither Galapagos nor Samoa data fall on any correlation line that might be defined by Hawaiian data.

**Figure 3.** Helium and Pb isotope systematics of basalts from the Reykjanes Ridge [Hilton et al. 2000] and Iceland [Breddam et al. 2000]. See text for discussion.

Figure 1

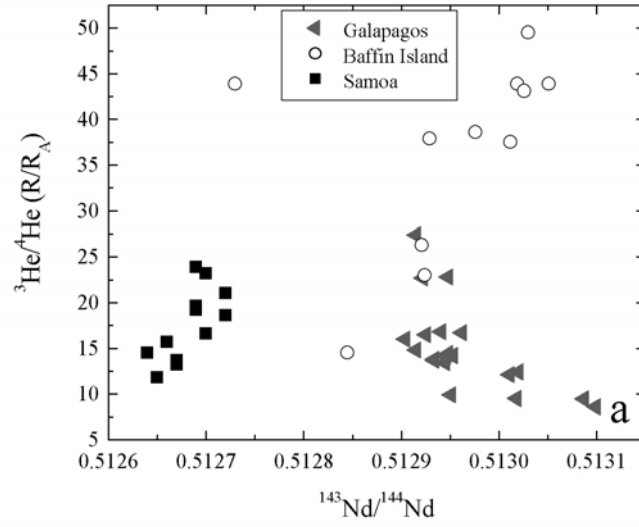


Figure 2

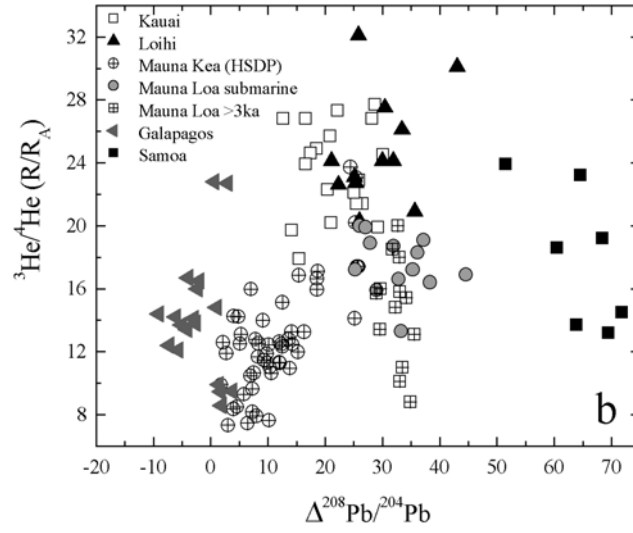
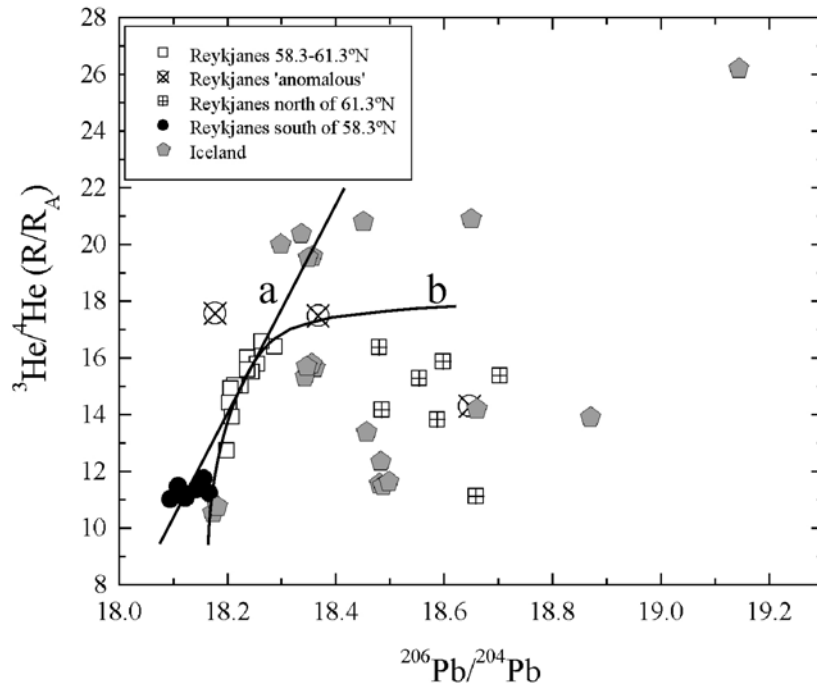


Figure 3



## References

- Albarède, F., 1998, Time-dependent models of U-Th-He and K-Ar evolution and the layering of mantle convection: *Chemical Geology*, v. 145, p. 413-429.
- , 2004, High  $^3\text{He}/^4\text{He}$  and solar Ne in OIB: Should we wonder?: *Geochimica et Cosmochimica Acta*, v. 68, p. A552.
- Albarède, F., and van der Hilst, R. D., 2002, Zoned mantle convection: *Phil. Trans. R. Soc. Lond. A.*, v. 360, p. 2569-2592.
- Allègre, C. J., 2002, The evolution of mantle mixing: *Phil. Trans. R. Soc. Lond. A.*, v. 360, p. 2411-2431.
- Allègre, C. J., Hofmann, A., and O'Nions, K., 1996, The Argon constraints on mantle structure: *Geophysical Research Letters*, v. 23, p. 3555-3557.
- Allègre, C. J., Staudacher, T., and Sarda, P., 1986, Rare gas systematics: formation of the atmosphere, evolution and structure of the Earth's mantle: *Earth and Planetary Science Letters*, v. 81, p. 127-150.
- Allègre, C. J., and Turcotte, D. L., 1985, Geodynamic mixing in the mesosphere boundary layer and the origin of oceanic islands: *Geophysical Research Letters*, v. 12, p. 207-210.
- , 1986, Implications of a two-component marble-cake mantle: *Nature*, v. 323, p. 123-127.
- Anderson, D. L., 1989, *Theory of the Earth*: Boston, Blackwell Scientific Publications, 366 p.
- , 1998a, The helium paradoxes: *Proceeding of the National Academy of Sciences USA*, v. 95, p. 4822-4827.
- , 1998b, A model to explain the various paradoxes associated with mantle noble gas geochemistry: *Proceeding of the National Academy of Sciences USA*, v. 95, p. 9087-9092.
- , 2000a, The Statistics and Distribution of Helium in the Mantle: *International Geology Review*, v. 42, p. 289-311.
- , 2000b, The Statistics of Helium Isotopes Along the Global Spreading Ridge System and the Central Limit Theorem: *Geophysical Research Letters*, v. 27, p. 2401-2404.
- , 2001, A statistical test of the two reservoir model for helium isotopes: *Earth and Planetary Science Letters*, v. 193, p. 77-82.
- , 2002, The Case for Irreversible Chemical Stratification of the Mantle: *International Geology Review*, v. 44, p. 97-116.
- Ballentine, C. J., and Burnard, P. G., 2002, Production, Release and Transport of Noble Gases in the Continental Crust, *in* Porcelli, D., Ballentine, C. J., and Wieler, R., eds., *Noble Gases in Geochemistry and Cosmochemistry*, Washington D. C., Geochemical Society & Mineralogical Society of America, p. 481-538.
- Ballentine, C. J., van Keken, P. E., Porcelli, D., and Hauri, E. H., 2002, Numerical models, geochemistry and the zero-paradox noble-gas mantle: *Phil. Trans. R. Soc. Lond. A.*, v. 360, p. 2611-2631.
- Batiza, R., 1984, Inverse relationship between Sr isotope diversity and rate of oceanic volcanism has implications for mantle heterogeneity: *Nature*, v. 309, p. 440-441.

- Becker, T. W., Kellogg, J. B., and O'Connell, R. J., 1999, Thermal constraints on the survival of primitive blobs in the lower mantle: *Earth and Planetary Science Letters*, v. 171, p. 351-365.
- Blichert-Toft, J., Weis, D., Maerschalk, C., Agranier, A., and Albarède, F., 2003, Hawaiian hot spot dynamics as inferred from the Hf and Pb isotope evolution of Mauna Kea volcano: *Geochemistry, Geophysics, Geosystems*, v. 4, p. 8704, doi:10.1029/2002GC000340.
- Bottinga, Y., and Javoy, M., 1990, MORB degassing: Bubble growth and ascent: *Chemical Geology*, v. 81, p. 255-270.
- Bracewell, R. N., 2000, *The Fourier Transform and its Applications*, McGraw-Hill, 616 p.
- Breddam, K., 2002, Kistufell: Primitive Melt from the Iceland Mantle Plume: *Journal of Petrology*, v. 43, p. 345-373.
- Breddam, K., Kurz, M. D., and Storey, M., 2000, Mapping out the conduit of the Iceland mantle plume with helium isotopes: *Earth and Planetary Science Letters*, v. 176, p. 45-55.
- Brooker, R. A., Du, Z., Blundy, J. D., Kelley, S. P., Allan, N. L., Wood, B. J., Chamorro, E. M., Wartho, J. A., and Purton, J. A., 2003a, The 'zero charge' partitioning behaviour of noble gases during mantle melting: *Nature*, v. 432, p. 738-741.
- Brooker, R. A., Heber, V., Kelley, S. P., and Wood, B. J., 2003b, Noble Gas Partitioning Behaviour During Mantle Melting: A Possible Explanation for 'The He Paradox?': *Eos. Trans. AGU*, v. 84, p. Fall Meet. Suppl., Abstract V31F-03.
- Brooker, R. A., Heber, V. S., Kelly, S. P., and Wood, B. J., 2004, Noble Gas Partitioning During Mantle Melting: Possible Retention of He & Ar relative to U, Th & K: *Lithos*, v. 73, p. S15.
- Burnard, P., Graham, D., and Farley, K., 2004, Fractionation of noble gases (He, Ar) during MORB mantle melting: a case study on the Southeast Indian Ridge: *Earth and Planetary Science Letters*, in press.
- Burnard, P. G., Graham, D. W., and Farley, K. A., 2002, Mechanisms of magmatic loss along the Southeast Indian Ridge and the Amsterdam-St. Paul Plateau: *Earth and Planetary Science Letters*, v. 203, p. 131-148.
- Butler, R., Sinton, J. M., Mahoney, J. J., and Smaglik, S. M., 1993, Spectral analysis of volcanic glass compositions from the East Pacific Rise Axis, 13°-23°S: *Journal of Geophysical Research*, v. 98, p. 11,851-11,864.
- Christiansen, R. L., Foulger, G. R., and Evans, J. R., 2002, Upper-Mantle Origin of the Yellowstone Hotspot: *GCA Bulletin*, v. 114, p. 1245-1256.
- Coltice, N., and Ricard, Y., 1999, Geochemical observations and one layer mantle convection: *Earth and Planetary Science Letters*, v. 174, p. 125-137.
- Coltice, N., and Richard, Y., 2002, On the origin of noble gases in mantle plumes: *Phil. Trans. R. Soc. Lond. A*, v. 360, p. 2633-2648.
- Dauphas, N., 2003, The dual origin of the terrestrial atmosphere: *Icarus*, v. 165, p. 326-339.
- Davies, G. F., 2002, Stirring geochemistry in mantle convection models with stiff plates and slabs: *Geochimica et Cosmochimica Acta*, v. 66, p. 3125-3142.
- DePaolo, D. J., 2004, He-3 and other isotopes in the lower mantle: the HSDP perspective: *Geochimica et Cosmochimica Acta*, v. 68, p. A556.

- DePaolo, D. J., Bryce, J. G., Dodson, A., Shuster, D. L., and Kennedy, B. M., 2001, Isotopic evolution of Mauna Loa and the chemical structure of the Hawaiian plume: *Geochemistry, Geophysics, Geosystems*, v. 2, doi:10.1029/2000GC000139.
- Dixon, E. T., Honda, M., McDougall, I., Campbell, I. A., and Sigurdsson, I., 2000, Preservation of near-solar neon isotopic ratios in Icelandic basalts: *Earth and Planetary Science Letters*, v. 180, p. 309-324.
- Dixon, J. E., Stolper, E. M., and Holloway, J. R., 1995, An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. 1. Calibration and solubility models: *Journal of Petrology*, v. 36, p. 1607-1631.
- Eiler, J. M., Farley, K. A., and Stolper, E. M., 1998, Correlated helium and lead isotope variations in Hawaiian lavas: *Geochimica et Cosmochimica Acta*, v. 62, p. 1977-1984.
- Eiler, J. M., Farley, K. A., Valley, J. W., Hofmann, A. W., and Stolper, E. M., 1996, Oxygen isotope constraints on the sources of Hawaiian volcanism: *Earth and Planetary Science Letters*, v. 144, p. 453-468.
- Eiler, J. M., Schiano, P., Kitchen, N., and Stolper, E. M., 1999, Oxygen-isotope evidence for recycled crust in the sources of mid-ocean-ridge basalts: *Nature*, v. 403, p. 530-534.
- Eisele, J., Abouchami, W., Galer, S. J. G., and Hofmann, A. W., 2003, The 320 kyr Pb isotope evolution of Mauna Kea lavas in the HSDP-2 drill core: *Geochemistry, Geophysics, Geosystems*, v. 4, doi:10.1029/2002GC000339.
- Farley, K. A., Basu, A. R., and Craig, H., 1993, He, Sr and Nd isotopic variations in lavas from the Juan Fernandez Archipelago, SE Pacific: *Contrib. Mineral. Petrol.*, v. 115, p. 75-87.
- Farley, K. A., Natland, J. H., and Craig, H., 1992, Binary mixing of enriched and undegassed (primitive?) mantle components (He, Sr, Nd, Pb) in Samoan lavas: *Earth and Planetary Science Letters*, v. 111, p. 183-199.
- Farley, K. A., and Neroda, E., 1998, Noble gases in the Earth's mantle: *Annual Review of Earth and Planetary Sciences*, v. 26, p. 189-218.
- Ferrachat, S., and Richard, Y., 2001, Mixing properties in the Earth's mantle: effects of the viscosity stratification and of oceanic crust segregation: *Geochemistry, Geophysics, Geosystems*, v. 2, doi:10.1029/2000GC000092.
- Fitton, J. G., and Dunlop, H. M., 1985, The Cameroon line, West Africa, and its bearing on the origin of oceanic and continental alkali basalt: *Earth and Planetary Science Letters*, v. 72, p. 23-38.
- Fornari, D. J., Perfit, M. R., Allan, J. F., and Batiza, R., 1985, Small-scale heterogeneities in depleted mantle sources: near-ridge seamount lava geochemistry and implications for mid-ocean ridge magmatic processes: *Nature*, v. 331, p. 511-513.
- Foulger, G. R., and al., e., 2001, Seismic tomography shows that upwelling beneath Iceland is confined to the upper mantle: *Geophysical Journal International*, v. 146, p. 504-530.
- Foulger, G. R., and Pearson, D. G., 2001, Is Iceland underlain by a plume in the lower mantle ? Seimology and helium isotopes: *Geophysical Journal International*, v. 145, p. F1-F5.

- Frey, F. A., Clague, D., Mahoney, J. J., and Sinton, J. M., 2000, Volcanism at the Edge of the Hawaiian Plume: Petrogenesis of Submarine Alkalic Lavas from the North Arch Volcanic Field: *Journal of Petrology*, v. 41, p. 667-691.
- Graham, D., Lupton, J., Albarède, F., and Condomines, M., 1990, A 360 000 year helium isotope record from Piton de la Fournaise, Réunion Island: *Nature*, v. 347, p. 545-548.
- Graham, D. W., 2002, Noble Gas Isotope Geochemistry of Mid-Ocean Ridge and Ocean Island Basalts: Characterization of Mantle Source Reservoirs, *in* Porcelli, D., Ballentine, C. J., and Wieler, R., eds., *Noble Gases in Geochemistry and Cosmochemistry*, Washington DC, Geochemical Society & American Society of America, p. 247-315.
- Graham, D. W., Castillo, P. R., Lupton, J. E., and Batiza, R., 1996, Correlated He and Sr isotope ratios in South Atlantic near-ridge seamounts and implications for mantle dynamics: *Earth and Planetary Science Letters*, v. 144, p. 491-503.
- Graham, D. W., Christie, D. M., Sharp, K. S., and Lupton, L. E., 1993, Mantle Plume Helium in Submarine Basalts from the Galápagos Platform: *Science*, v. 262, p. 2023-2026.
- Graham, D. W., Lupton, J. E., Spera, F. J., and Christie, D. M., 2001, Upper-mantle dynamics revealed by helium isotope variations along the southeast Indian Ridge: *Nature*, v. 409, p. 701-703.
- Grand, S. P., 1994, Mantle shear structure beneath the Americas and surrounding oceans: *Journal of Geophysical Research*, v. 99, p. 11,591-11,621.
- Hanan, B. B., and Graham, D. W., 1996, Lead and Helium Isotope Evidence from Oceanic Basalts for a Common Deep Source of Mantle Plumes: *Science*, v. 272, p. 991-995.
- Hanyu, T., Clague, D., Kaneoka, I., Dunai, T. J., and Davies, G. R., 2004, Noble gas systematics of submarine alkalic lavas in the Hawaiian hotspot: *Chemical Geology*, in press.
- Harlou, R., Kent, A. J. R., Breddam, K., Davidson, J. P., and Pearson, D. G., 2004, Origin of extreme  $^3\text{He}/^4\text{He}$  signatures in Icelandic lavas: Insights from melt inclusion studies: *Geochimica et Cosmochimica Acta*, v. 68, p. A579.
- Hart, S. R., 1984, A large-scale isotope anomaly in the Southern Hemisphere mantle: *Nature*, v. 309, p. 753-757.
- Hart, S. R., Hauri, E. H., Oschmann, L. A., and Whitehead, J. A., 1992, Mantle Plumes and Entrainment: Isotopic Evidence: *Science*, v. 256, p. 517-520.
- Hauri, E., Whitehead, J. A., and Hart, S. R., 1994, Fluid dynamic and geochemical aspects of entrainment in mantle plumes: *Journal of Geophysical Research*, v. 99, p. 24,275-24,300.
- Hauri, E. K., 1996, Major element variability in the Hawaiian mantle plume: *Nature*, v. 382, p. 415-419.
- Helffrich, G. R., and Wood, B. J., 2001, The Earth's Mantle: *Nature*, v. 412, p. 501-507.
- Hilton, D. R., Barling, J., and Wheller, G. E., 1995, Effect of shallow-level contamination on the helium isotope systematics of ocean-island lavas: *Nature*, v. 373, p. 330-333.

- Hilton, D. R., Thirlwall, M. F., Taylor, R. N., Murton, B. J., and Nichols, A., 2000, Controls on magmatic degassing along the Reykjanes Ridge with implications for the helium paradox: *Earth and Planetary Science Letters*, v. 183, p. 43-50.
- Hofmann, A. W., 1997, Mantle geochemistry: the message from oceanic volcanism: *Nature*, v. 385, p. 219-229.
- Honda, M., McDougall, I., Patterson, D. B., Doulgeris, A., and Clague, D. A., 1993, Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii: a solar component in the Earth: *Geochimica et Cosmochemica Acta*, v. 57, p. 859-874.
- Hunt, D. L., and Kellogg, L. H., 2001, Quantifying mixing and age variations of heterogeneities in models of mantle convection: role of depth-dependent viscosity: *Journal of Geophysical Research*, v. 106, p. 6747-6759.
- Ito, G., and Mahoney, J. J., 2004, Flow and melting of a heterogeneous mantle: 2. Implications for a chemically zoned non-layered mantle: *Earth and Planetary Science Letters*, in press.
- Kaneoka, I., and Takaoka, N., 1978, Excess  $^{129}\text{Xe}$  and high  $^3\text{He}/^4\text{He}$  ratios in olivine phenocrysts of kapuho lava and xenolithic dunites from Hawaii: *Earth and Planetary Science Letters*, v. 39, p. 382-386.
- Kellogg, J. B., Jacobsen, S. B., and O'Connell, R. J., 2002, Modeling the distribution of isotopic ratios in geochemical reservoirs: *Earth and Planetary Science Letters*, v. 204, p. 183-202.
- Kellogg, L. H., Hager, B. H., and van der Hilst, R. D., 1999, Compositional Stratification in the Deep Mantle: *Science*, v. 283, p. 1881-1884.
- Kellogg, L. H., and Wasserburg, G. J., 1990, The role of plumes in mantle helium fluxes: *Earth and Planetary Science Letters*, v. 99, p. 276-289.
- Kogiso, T., Hirshmann, M., and Reiners, P. W., 2004, Length scales of mantle heterogeneities and their relationship to ocean island basalt chemistry: *Geochimica et Cosmochemica Acta*, v. 68, p. 345-360.
- Kurz, M. D., Curtice, J., III, D. E. L., and Solow, A., 2004, Rapid helium isotopic variability in Mauna Kea shield lavas from the Hawaiian Scientific Drilling Project: *Geochemistry, Geophysics, Geosystems*, v. 5, doi:10.1029/2002GC000439.
- Kurz, M. D., and Geist, D., 1999, Dynamics of the Galapagos hotspot from helium isotope geochemistry: *Geochimica et Cosmochemica Acta*, v. 63, p. 4139-4156.
- Kurz, M. D., Kenna, T. C., Lassiter, J. C., and DePaolo, D. J., 1996, Helium isotopic evolution of Mauna Kea Volcano: First results from the 1 km drill core: *Journal of Geophysical Research*, v. 101, p. 11,781-11,791.
- Lassiter, J. C., Blichert-Toft, J., Hauri, E. H., and Barscuzs, H. G., 2003, Isotope and trace element variations in lavas from Raivavae and Rapa, Cook-Austral islands: constraints on the nature of HIMU- and EM-mantle and the origin of mid-plate volcanism in French Polynesia: *Chemical Geology*, v. 202, p. 115-138.
- Lee, C.-T., 2004, Are Earths Core and Mantle on Speaking Terms?: *Science*, v. 306, p. 64-65.
- Marty, B., and Zimmermann, L., 1999, Volatiles (He, C, N, Ar) in mid-ocean ridge basalts: Assessments of shallow-level fractionation and characterization of source composition: *Geochimica et Cosmochemica Acta*, v. 63, p. 3619-3633.

- Matsumoto, T., Seta, A., Matsuda, J., Takebe, M., Chen, Y., and Arai, S., 2002, Helium in the Archean komatiites revisited: significantly high  $^3\text{He}/^4\text{He}$  ratios revealed by fractional crushing gas extraction: *Earth and Planetary Science Letters*, v. 196, p. 213-225.
- Meibom, A., and Anderson, D. L., 2003, The Statistical Upper Mantle Assemblage: *Earth and Planetary Science Letters*, v. 217, p. 123-139.
- Meibom, A., Anderson, D. L., Sleep, N. H., Frei, R., Chamberlain, C. P., Hren, M. T., and Wooden, J. L., 2003, Are high  $^3\text{He}/^4\text{He}$  ratios in oceanic basalts an indicator of deep-mantle plume components?: *Earth and Planetary Science Letters*, v. 208, p. 197-204.
- Meibom, A., Sleep, N. H., Chamberlain, C. P., Coleman, R. G., Frei, R., Hren, M. T., and Wooden, J. L., 2002, Re-Os isotopic evidence for long-lived heterogeneity and equilibrium processes in Earth's upper mantle: *Nature*, v. 419, p. 705-708.
- Montelli, R., Nolet, G., Dahlen, F. A., Masters, G., Engdahl, E. R., and Hung, S.-H., 2004, Finite-Frequency Tomography Reveals a Variety of Plumes in the Mantle: *Science*, v. 303, p. 338-343.
- Moreira, M., Breddam, K., Curtice, J., and Kurz, M. D., 2001, Solar neon in the Icelandic mantle: new evidence for an undegassed lower mantle: *Earth and Planetary Science Letters*, v. 185, p. 15-23.
- Moreira, M., Doucelance, R., Kurz, M. D., Dupré, B., and Allègre, C. J., 1999, Helium and lead isotope geochemistry of the Azores Archipelago: *Earth and Planetary Science Letters*, v. 169, p. 189-205.
- Moreira, M., and Sarda, P., 2000, Noble gas constraints on degassing processes: *Earth and Planetary Science Letters*, v. 176, p. 375-386.
- Moreira, M., Staudacher, T., Sarda, P., Schilling, J.-G., and Allègre, C. J., 1995, A primitive plume neon component in MORB: The Shona ridge-anomaly, South Atlantic (51-52°S): *Earth and Planetary Science Letters*, v. 133, p. 367-377.
- Morgan, J. P., 2001, Thermodynamics of pressure release melting of a veined plum pudding mantle: *Geochemistry, Geophysics, Geosystems*, v. 2, doi:10.1029/2000GC000049.
- Morgan, J. P., and Morgan, W. J., 1999, Two-stage melting and the geochemical evolution of the mantle: a recipe for mantle plum-pudding: *Earth and Planetary Science Letters*, v. 170, p. 215-239.
- Mukhopadhyay, S., Lassiter, J. C., Farley, K. A., and Bogue, S. W., 2003, Geochemistry of Kauai shield-stage lavas: Implications for the chemical evolution of the Hawaiian plume: *Geochemistry, Geophysics, Geosystems*, v. 4, doi:10.1029/2002GC000342.
- Natland, J. H., 2003, Capture of Helium and Other Volatiles during the Growth of Olivine Phenocrysts in Picritic Basalts from the Juan Fernandez Islands: *Journal of Petrology*, v. 44, p. 421-456.
- Niedermann, S., Bach, W., and Erzinger, J., 1997, Noble gas evidence for a lower mantle component in MORBs from the southern East Pacific Rise: Decoupling of helium and neon isotope systematics: *Geochimica et Cosmochimica Acta*, v. 61, p. 2697-2715.

- Nuccio, P. M., and Panoita, A., 2000, Investigation of the noble gas solubility in H<sub>2</sub>O-CO<sub>2</sub> bearing silicate liquids at moderate pressure II: the extended ionic porosity (EIP) model: *Earth and Planetary Science Letters*, v. 183, p. 499-512.
- O'Nions, R. K., and Oxburgh, E. R., 1983, Heat and helium in the Earth: *Nature*, v. 306, p. 429-431.
- Ozima, M., 1994, Noble gas state in the mantle: *Reviews of Geophysics*, v. 32, p. 405-426.
- Ozima, M., and Podosek, F. A., 2002, *Noble Gas Geochemistry*: Cambridge University Press, 286 p.
- Pepin, R. O., and Porcelli, D., 2002, Origin of Noble Gases in the Terrestrial Planets, *in* Porcelli, D., Ballentine, C. J., and Wieler, R., eds., *Noble Gases in Geochemistry and Cosmochemistry*, Washington D. C., Geochemical Society & American Society of America, p. 191-246.
- Porcelli, D., and Ballentine, C. J., 2002, Models for the Distribution of Terrestrial Noble Gases and Evolution of the Atmosphere, *in* Porcelli, D., Ballentine, C. J., and Wieler, R., eds., *Noble Gases in Geochemistry and Cosmochemistry: Reviews in Mineralogy and Geochemistry*, Washington D. C., Geochemical Society & Mineralogical Society of America, p. 411-480.
- Porcelli, D., Ballentine, C. J., and Wieler, R., 2002, Noble Gases in Geochemistry and Cosmochemistry: *Reviews in Mineralogy and Geochemistry*, v. 47: Washington D.C., Geochemical Society & Mineralogical Society of America, 844 p.
- Porcelli, D., and Halliday, A. N., 2001, The core as a possible source of mantle helium: *Earth and Planetary Science Letters*, v. 192, p. 45-56.
- Porcelli, D., and Wasserburg, G. J., 1995, Mass transfer of helium, neon, argon, and xenon through a steady-state upper mantle: *Geochimica et Cosmochimica Acta*, v. 59, p. 4921-4937.
- Poreda, R., Schilling, J.-G., and Craig, H., 1986, Helium and hydrogen isotopes in ocean-ridge basalts north and south of Iceland: *Earth and Planetary Science Letters*, v. 78, p. 1-17.
- Reisberg, L., and Zindler, A., 1986, Extreme isotopic variability in the upper mantle: evidence from Ronda: *Earth and Planetary Science Letters*, v. 81, p. 29-45.
- Rudge, J. F., McKenzie, D., and Haynes, P. H., 2004, A theoretical approach to understanding the isotopic heterogeneity of mid-ocean ridge basalt: *Geochimica et Cosmochimica Acta*, in press.
- Salters, V. J. M., and Stracke, A., 2004, Composition of the depleted mantle: *Geochemistry, Geophysics, Geosystems*, v. 5, doi:10.1029/2003GC000597.
- Sarda, P., and Moreira, M., 2002, Vesiculation and vesicle loss in mid-ocean ridge glasses: He, Ne, Ar elemental fractionation and pressure influence: *Geochimica et Cosmochimica Acta*, v. 66, p. 1449-1458.
- Sarda, P., Moreira, M., Staudacher, T., Schilling, J.-G., and Allègre, C. J., 2000, Rare gas systematics on the southernmost Mid-Atlantic Ridge: Constraints on the lower mantle and the Dupal source: *Journal of Geophysical Research*, v. 105, p. 5973-5996.
- Schaefer, B. F., Turner, S., Parkinson, I., Rogers, N., and Hawkesworth, C., 2002, Evidence for recycled Archean oceanic mantle lithosphere in the Azores plume: *Nature*, v. 420, p. 304-307.

- Schlosser, P., and Winckler, G., 2002, Noble Gases in Ocean Waters and Sediments, *in* Porcelli, D., Ballentine, C. J., and Wieler, R., eds., *Noble Gases in Geochemistry and Cosmochemistry*, Washington D. C., Geochemical Society & American Society of America, p. 701-730.
- Sleep, N. H., 1979, Thermal History and Degassing of the Earth: Some simple Calculations: *Journal of Geology*, v. 87, p. 671-686.
- Stolper, E., Sherman, S., Garcia, M., Maker, M., and Seaman, C., 2004, Glass in the submarine section of the HSDP2 drill core, Hilo, Hawaii: *Geochemistry, Geophysics, Geosystems*, v. 5, doi:10.1029/2003GC000553.
- Stuart, F. M., and Ellam, R. M., 2004, HRDM: The common high  $^3\text{He}/^4\text{He}$  reservoir in Earth mantle: *Geochimica et Cosmochimica Acta*, v. 68, p. A555.
- Stuart, F. M., Lass-Evans, S., Fitton, J. G., and Ellam, R. M., 2003, High  $^3\text{He}/^4\text{He}$  ratios in picritic basalts from Baffin Island and the role of a mixed reservoir in mantle plumes: *Nature*, v. 424, p. 57-59.
- Tackley, P. J., 2000, Mantle Convection and Plate Tectonics: Toward and Integrated Physical and Chemical Theory: *Science*, v. 288, p. 2002-2007.
- Tolstikhin, I., and Hofmann, A. W., 2004, Early crust on top of the Earth's core: *Physics of the Earth and Planetary Interiors*, in press.
- Tolstikhin, I. N., and Marty, B., 1998, The evolution of terrestrial volatiles: a view from helium, neon, argon and nitrogen isotope modelling: *Chemical Geology*, v. 147, p. 27-52.
- Trieloff, M., Kunz, J., Clague, D. A., Harrison, D., and Allègre, C. J., 2000, The nature of pristine noble gases in mantle plumes: *Science*, v. 288, p. 1036-1038.
- Valbracht, P. J., Staudigel, H., Honda, M., McDougall, I., and Davies, G. R., 1996, Isotopic tracing of volcanic source regions from Hawaii: decoupling of gaseous from lithophile magma components: *Earth and Planetary Science Letters*, v. 144, p. 185-198.
- van der Hilst, R. D., Widiyantoro, S., and Engdahl, R., 1997, Evidence for deep mantle circulation from global tomography: *Nature*, v. 386, p. 578-584.
- van Keken, P. E., and Ballentine, C. J., 1998, Whole-mantle versus layered convection and the role of a high-viscosity lower mantle in terrestrial volatile evolution: *Earth and Planetary Science Letters*, v. 156, p. 19-32.
- , 1999, Dynamical models of mantle volatile evolution and the role of phase transitions and temperature dependent rheology: *Journal of Geophysical Research*, v. 104, p. 7137-7151.
- van Keken, P. E., Ballentine, C. J., and Porcelli, D., 2001, A dynamical investigation of the heat and helium imbalance: *Earth and Planetary Science Letters*, v. 188, p. 421-434.
- van Keken, P. E., Hauri, E., and Ballentine, C. J., 2002, Mantle Mixing: The Generation, Preservation, and Destruction of Chemical Heterogeneity: *Annual Review of Earth and Planetary Sciences*, v. 30, p. 493-525.
- Wetherill, G. W., 1954, Variations in the isotope abundances of neon and argon extracted from radioactive minerals: *Physical Review*, v. 96, p. 679-683.
- Williams, Q., and Hemley, R. J., 2001, Hydrogen in the Deep Earth: *Annual Review of Earth and Planetary Sciences*, v. 29, p. 365-418.

- Woodhead, J. D., and McCulloch, M. T., 1989, Ancient seafloor signals in Pitcairn Island lavas and evidence for large amplitude, small length-scale mantle heterogeneities: *Earth and Planetary Science Letters*, v. 94, p. 257-273.
- Workman, R. K., Hart, S. R., Jackson, M., Regelous, M., Farley, K. A., Blusztajn, J., Kurz, M., and Staudigel, H., 2004, Recycled metasomatized lithosphere as the origin of the Enriched Mantle II end-member: Evidence from the Samoan Volcanic Chain: *Geochemistry, Geophysics, Geosystems*, v. 5, doi:10.1029/2003GC000632.
- Xie, S., and Tackley, P. J., 2004, Evolution of Helium and Argon Isotopes in a Convecting Mantle: *Physics of the Earth and Planetary Interiors*, v. 146, p. 417-439.
- Yamamoto, J., and Burnard, P. G., 2004, Solubility controlled noble gas fractionation during magmatic degassing: implications for noble gas compositions of primary melts of OIB and MORB: *Geochimica et Cosmochimica Acta*, in press.
- Yatsevich, I., and Honda, M., 1997, Production of nucleogenic neon in the Earth from natural radioactive decay: *Journal of Geophysical Research*, v. 102, p. 10,291-10,298.
- Yokochi, R., and Marty, B., 2004, A determination of the neon isotopic composition of the deep mantle: *Earth and Planetary Science Letters*, v. 225, p. 77-88.
- Zahnle, K., Kastings, J. F., and Pollack, J. B., 1990, Mass fractionation of noble gases in diffusion-limited hydrodynamic hydrogen escape: *Icarus*, v. 84, p. 502-527.
- Zindler, A., and Hart, S., 1986, Chemical Geodynamics: *Annual Review of Earth and Planetary Sciences*, v. 14, p. 493-571.
- Zindler, A., Staudigel, H., and Batiza, R., 1984, Isotope and trace element geochemistry of young Pacific seamounts: implications for the scale of upper mantle heterogeneity: *Earth and Planetary Science Letters*, v. 70, p. 175-195.