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# Heterogeneities from the first 100 million years recorded in deep mantle noble gases from the Northern Lau Back-arc Basin

Maria K. Pető<sup>a,\*</sup>, Sujoy Mukhopadhyay<sup>a</sup>, Katherine A. Kelley<sup>b</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA

<sup>b</sup> Graduate School of Oceanography, University of Rhode Island, Narragansett, RI, USA

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## ABSTRACT

Heavy noble gases can record long-lasting heterogeneities in the mantle, because Ne, Ar, and Xe isotopes are produced from extant (U, Th, K) and extinct ( $^{129}\text{I}$  and  $^{244}\text{Pu}$ ) radionuclides. However, the presence of ubiquitous atmospheric contamination in basalts, particularly for ocean island basalts (OIBs) that sample the Earth's deep mantle, have largely hampered precise characterization of the mantle source compositions. Here we present new high-precision noble gas data from gas-rich basalts erupted along the Rochambeau Rift (RR) in the northwestern corner of the Lau Basin. The strong influence of a deep mantle plume in the Rochambeau source is apparent from low  $^4\text{He}/^3\text{He}$  ratios down to 25,600 ( $^3\text{He}/^4\text{He}$  of 28.1 $R_A$ ).

We find that the Rochambeau source is characterized by low ratios of radiogenic to non-radiogenic nuclides of Ne, Ar, and Xe (i.e., low  $^{21}\text{Ne}/^{22}\text{Ne}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$ , and  $^{129}\text{Xe}/^{130}\text{Xe}$ ) compared to the mantle source of mid-ocean ridge basalts (MORBs). High-precision xenon isotopic measurements indicate that the lower  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios in the Rochambeau source cannot be explained solely by mixing atmospheric xenon with MORB-type xenon; nor can fission-produced Xe be added to MORB Xe to produce the compositions seen in the Rochambeau basalts. Deconvolution of fissionogenic xenon isotopes demonstrate a higher proportion of Pu-fission derived Xe in the Rochambeau source compared to the MORB source. Therefore, both I/Xe and Pu/Xe ratios are different between OIB and MORB sources. Our observations require heterogeneous volatile accretion and a lower degree of processing for the plume source compared to the MORB source. Since differences in  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios have to be produced while  $^{129}\text{I}$  is still alive, OIB and MORB sources must have been processed at different rates for the first 100 million years (Myr) of Solar System history, and subsequent to this period, the two reservoirs have not been homogenized.

In combination with recent results from the Iceland plume, our noble gas observations require the formation and preservation of less-degassed, early-formed (pre-4.45 Ga) heterogeneities in the Earth's deep mantle. Consequently, the primitive noble gas reservoir sampled by mantle plumes cannot be created solely through sequestration of recycled slabs or undegassed melts at the base of the mantle during the past 4.4 Ga. Finally, if the more primitive, less degassed heterogeneities reside in the Large Low Shear Wave Velocity Provinces (LLSVPs), then LLSVPs must be long-lasting features of the deep mantle and are not composed exclusively of recycled material.

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## 1. Introduction

The noble gas compositions of mantle-derived basalts provide information on the degassing history, style of mantle convection, and volatile exchange between the deep Earth and the atmosphere. Compared to mid-ocean ridge basalts (MORBs), ocean island basalts (OIBs) from Iceland, Hawaii, Galapagos, Réunion and Samoa are characterized by lower ratios of radiogenic to

primordial isotopes such as  $^4\text{He}/^3\text{He}$ ,  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  (e.g., Hanyu et al., 2001; Honda et al., 1993a; Mukhopadhyay, 2012; Poreda and Farley, 1992; Raquin and Moreira, 2009; Trieloff et al., 2000; Trieloff et al., 2002). Likewise, lower ratios of radiogenic to non-radiogenic Xe isotopes ( $^{129}\text{Xe}/^{130}\text{Xe}$ ) are found in Hawaii, Samoa, Iceland and Reunion (e.g., Mukhopadhyay, 2012; Poreda and Farley, 1992; Trieloff et al., 2000; Trieloff et al., 2002; Hopp and Trieloff, 2005). These noble gas signatures in OIBs are commonly attributed to sampling parts of Earth's mantle that are significantly less degassed than the MORB source (e.g., Allègre et al., 1987, 1996; Graham, 2002; Gonnermann and Mukhopadhyay, 2009; Kurz et al., 1982; Kurz et al., 2009; Porcelli and Wasserburg,

\* Corresponding author. Tel.: +1 8574882594.

E-mail address: [mpeto@fas.harvard.edu](mailto:mpeto@fas.harvard.edu) (M.K. Pető).

1995; Staudacher and Allègre, 1982). Shallow-level atmospheric contamination, however, often makes it difficult to decipher whether the lower measured Ar and Xe isotopic ratios in OIBs are indeed reflective of the mantle source composition. Additionally, the low  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios in OIBs may arise from recycled atmospheric Ar and Xe and not from a less degassed reservoir (Holland and Ballentine, 2006; Kendrick et al., 2011; Trierloff and Kunz, 2005).

If the low  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios in OIBs are indeed from a less degassed reservoir, then the OIB and MORB reservoirs must be partially isolated from each other since 4.45 Ga as  $^{129}\text{I}$ , which produces  $^{129}\text{Xe}$ , became extinct 100 Myr after the start of the Solar System. Such long-term separation would invalidate many models put forth to explain the chemical and dynamical evolution of the mantle. On the other hand, if the differences in  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios between OIBs and MORBs arise solely from recycling of atmospheric Xe, long-term separation of the two sources is not required and extensive mixing between the sources may be allowed. Hence, addressing the origin of the low  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios observed in OIBs compared to MORBs is of fundamental importance in understanding whether compositional heterogeneities dating back to Earth's accretion are still preserved. The preservation of old heterogeneities in the deep mantle can in turn provide important constraints on long-term mixing rates and mass flow in the mantle.

Recently, Mukhopadhyay (2012) and Tucker et al. (2012) demonstrated that the lower  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  in the Iceland plume compared to depleted MORBs cannot be generated solely through recycling of atmospheric noble gases. To investigate whether the composition of the Iceland plume is representative of other mantle plumes, we present combined He–Ne–Ar–Xe measurements in gas-rich basaltic glasses from the Rochambeau Rift in the northern Lau Back-arc Basin with  $^4\text{He}/^3\text{He}$  ratios as low as 25,600 ( $28.1R_A$ , where  $R_A$  is the  $^3\text{He}/^4\text{He}$  ratio normalized to the atmospheric ratio of  $1.39 \times 10^{-6}$ ).

The RR is located in the northwestern flank of the Lau Back-arc Basin, behind the Tonga arc, in the western Pacific (Fig. 1). Shear-wave splitting analyses suggest a fast direction of anisotropy that is oriented north to south in the Lau back-arc spreading center (Smith et al., 2001). If this anisotropy is interpreted in terms of mantle flow, it would suggest southward flow of the Pacific mantle (Smith et al., 2001). Slab rollback could induce the southward flow, which would consequently introduce Samoan plume material into the northern Lau back-arc region (Smith et al., 2001; Regelous et al. 2008; Jackson et al., 2010) through a tear in the Tonga slab beneath the Vitiiaz lineament (Millen and Hamburger, 1998).

The flow of Samoan plume material into the northern Lau Basin is consistent with observations of low  $^4\text{He}/^3\text{He}$  ratios along the RR, while  $^4\text{He}/^3\text{He}$  ratios in the central and southern Lau Basin are consistently MORB-like (Poreda and Craig, 1992; Lupton et al., 2009; Turner and Hawkesworth, 1998; Hahm et al., 2012; Honda et al., 1993b; Hilton et al., 1993). For example,  $^4\text{He}/^3\text{He}$  ratios along the RR are as low as 32,700–25,600 ( $22$ – $28.1R_A$ ; Hahm et al., 2012; Poreda and Craig, 1992; Lupton et al., 2009). These values are similar to the lowest reported  $^4\text{He}/^3\text{He}$  ratio of 21,000 from Samoa ( $34.2R_A$ , Jackson et al., 2007; Farley et al., 1992).  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios of up to  $11,988 \pm 156$  and  $7.04 \pm 0.1$ , respectively, have been measured in Samoan mantle xenoliths (Poreda and Farley, 1992). Consequently, if Samoan plume material influences the He isotopic composition of basalts along the RR, non-atmospheric, but low  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios should be expected in these basalts. Thus, basaltic glasses from the RR could be ideal for characterizing the heavy noble gas composition of a low  $^4\text{He}/^3\text{He}$  mantle plume. In this study, we use combined He–Ne–Ar–Xe measurements in basaltic glass samples

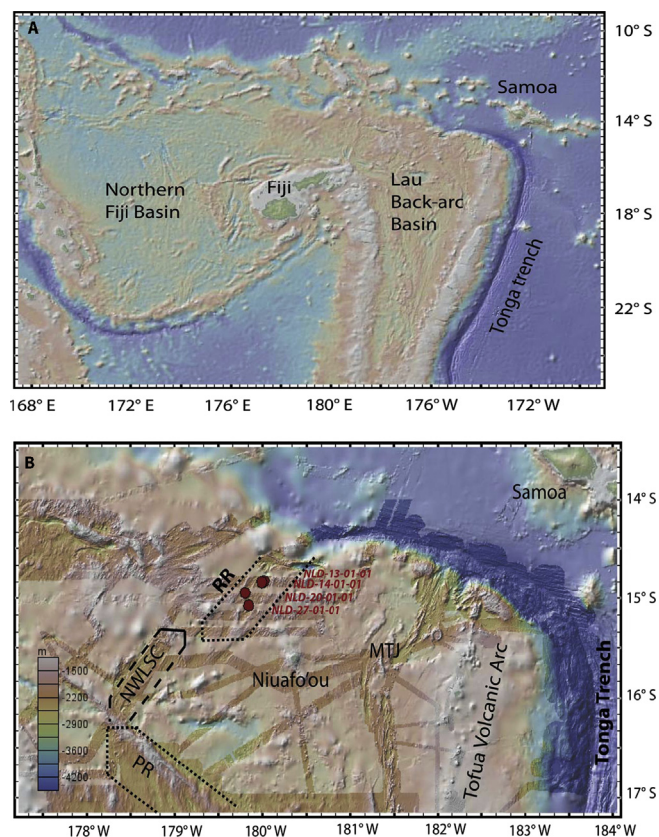


Fig. 1. (A) Regional bathymetric map of the Western Pacific and (B) bathymetric map of the Lau Basin showing the location of the four studied samples (RR=Rochambeau Rift, NWLSC=Northwest Lau Spreading Center, PR=Peggy Ridge, MTJ=Mangatolu Triple Junction).

to constrain the Ne, Ar and Xe isotopic composition of the RR mantle. We use the mantle source composition from Rochambeau to investigate whether the lower  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios measured in plumes can be assigned to recycled atmospheric noble gases. Additionally, we utilize our Xe isotopic measurements to constrain the age of heterogeneities sampled by deep mantle plumes, and test whether dynamical and chemical evolution models of the mantle are consistent with our new observations.

## 2. Analytical methods

We analyzed four basaltic glass samples from the Rochambeau Rift: NLD-13-01-01, NLD-14-01-01, NLD-20-01-01 and NLD-27-01-01 (abbreviated as NLD-13, NLD-14, NLD-20, and NLD-27 in the following text; Fig. 1). The samples were pillow lavas that were collected by dredging during the voyage SS07/2008 of the R/V Southern Surveyor (Lupton et al., 2009; Lytle et al., 2012).  $^4\text{He}/^3\text{He}$  ratios of the four samples were previously measured by Lupton et al. (2009) and range between 25,600 and 46,700 ( $15.4R_A$ – $28.1R_A$ ). Glass chunks were carefully selected to avoid phenocrysts. In order to remove surface alteration, glasses were leached in 2% nitric acid for 10–20 min, and then ultrasonically cleaned in distilled water and acetone. Single pieces of basaltic glass (3.2–6.8 g) were baked under vacuum for 24 h at 100 °C and were pumped for an additional 6–12 days. Samples were crushed in vacuo using a hydraulic ram to release magmatic gases trapped in vesicles. The released gases were purified by sequential exposure to hot and cold SAES getters and a small split of the gas was let into a quadrupole mass spectrometer to determine the

Ar abundance and an approximate  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio. The noble gases were then trapped on a cryogenic cold-finger. He was separated from Ne at 33 K and let into the Nu Noblesse mass spectrometer. The measurements were carried out at 250  $\mu\text{A}$  trap current and an electron accelerating voltage of 60 eV. The three Ne isotopes were simultaneously detected on three discrete dynode multipliers operating in pulse counting mode.  $^{20}\text{Ne}$  beams larger than 100,000 Hz were measured on a Faraday cup. An automated liquid nitrogen trap was used to keep the Ar and  $\text{CO}_2$  backgrounds low and we corrected for isobaric interferences from doubly-charged Ar and  $\text{CO}_2$ . The  $^{40}\text{Ar}^{++}/^{40}\text{Ar}^+$  and  $\text{CO}_2^{++}/\text{CO}_2^+$  ratios were  $0.031 \pm 0.003$  and  $0.0045 \pm 0.0005$ , respectively, and the  $^{40}\text{Ar}^{++}$  and  $\text{CO}_2^{++}$  corrections were all below 1%. For Ar, depending on the abundance measured by the quadrupole mass spectrometer, a fraction of the gas was let into the mass spectrometer. Isotopes were measured simultaneously using the Faraday for  $^{40}\text{Ar}$  and the axial and low mass multipliers for  $^{38}\text{Ar}$  and  $^{36}\text{Ar}$ , respectively. Xe was measured using the three discrete dynode multipliers in a combination of multicollection and peak jumping mode. Additional analytical details are described in Mukhopadhyay (2012).

Measured blanks of  $^4\text{He}$ ,  $^{22}\text{Ne}$ ,  $^{36}\text{Ar}$  and  $^{130}\text{Xe}$  were all below  $1.5 \times 10^{-11}$ ,  $1.1 \times 10^{-13}$ ,  $8.1 \times 10^{-13}$ , and  $1.3 \times 10^{-16}$   $\text{cm}^3$  STP, respectively, and were typically a factor of 2 lower. Blanks had isotopic ratios that were statistically undistinguishable from atmospheric values. Since the bubbles trapped in the glass themselves have a post-eruptive air contaminant, no blank corrections were applied to the sample isotopic ratios. Mass discrimination for He was corrected using the HH3 standard with a  $^4\text{He}/^3\text{He}$  ratio of 81,700 ( $8.81R_A$ ; Gayer et al., 2008) and Ne, Ar, and Xe were corrected using air as a standard. Mass discrimination was monitored using sample-standard bracketing with additional standards run overnight. The reproducibility of the standards was used to determine the reported  $1\sigma$  uncertainty.

### 3. Results

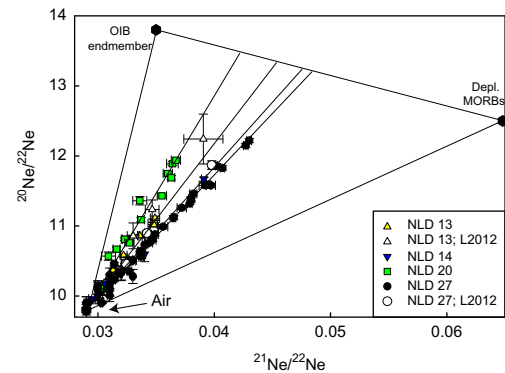
We performed between 13 and 45 step-crushes for each sample. The He, Ne, Ar and Xe abundance and isotopic data are presented in Supplemental Tables 1 and 2.

#### 3.1. Measured Ne, Ar and Xe isotopic ratios

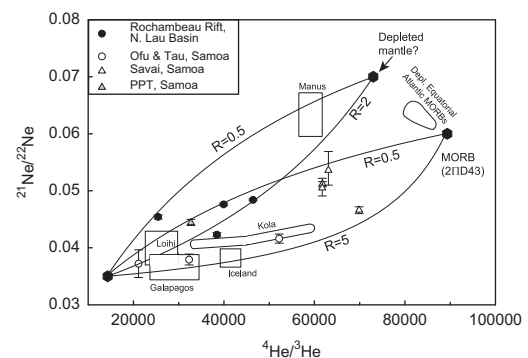
We measured  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios of up to  $12.22 \pm 0.03$  ( $1\sigma$ ) and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios up to  $0.0430 \pm 0.0002$  ( $1\sigma$ ) in the NLD-27 sample with a  $^4\text{He}/^3\text{He}$  ratio of 46,700 ( $15.4R_A$ ). Measured  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios reach  $9269 \pm 93$  ( $1\sigma$ ) in the same sample, which is close to the maximum measured  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of  $11,988 \pm 156$  at the PPT seamount off Samoa (Poreda and Farley, 1992). The maximum measured  $^{40}\text{Ar}/^{36}\text{Ar}$  value in NLD-13, which has a  $^4\text{He}/^3\text{He}$  ratio of 25,600 ( $28.1R_A$ ) is  $4828 \pm 48$ . We find measured  $^{129}\text{Xe}/^{130}\text{Xe}$  excesses with respect to the atmospheric composition in all 4 of the Rochambeau samples. The highest measured  $^{129}\text{Xe}/^{130}\text{Xe}$  is  $6.93 \pm 0.03$  ( $1\sigma$ ) from NLD-13 and represents the largest excess yet recorded in a basalt with a  $^4\text{He}/^3\text{He}$  ratio as low as 25,600 (Supplemental Table 2).

#### 3.2. Ne, Ar and Xe isotopic composition of the Rochambeau Rift mantle source

Shallow-level air contamination affects all Ne, Ar, and Xe isotopic measurements in mantle-derived basalts (e.g., Sarda et al., 1985; Honda et al., 1993a; Valbracht et al., 1997; Moreira et al., 1998; Farley and Neroda, 1998). In order to accurately interpret differences in noble gas compositions of mantle

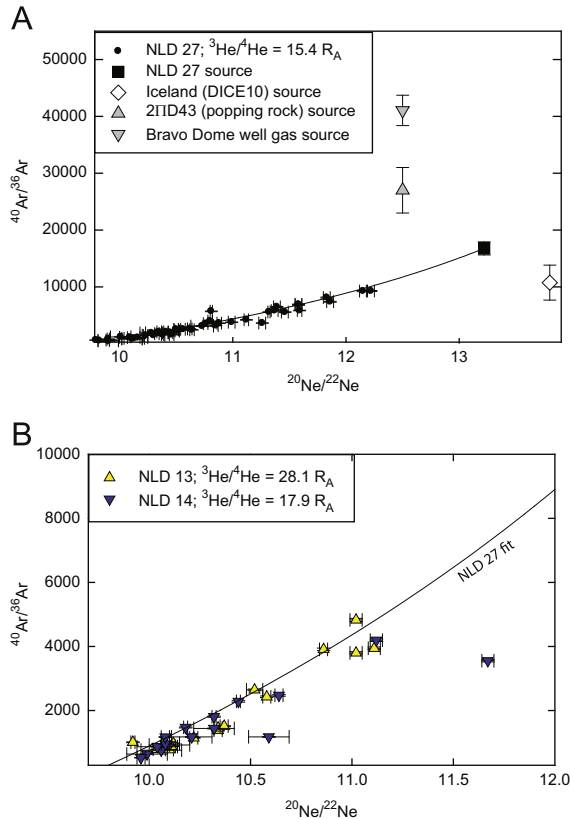


**Fig. 2.** Neon three isotope plot for samples from the Rochambeau Rift. Each point represents the Ne isotopic composition of a crush step. Error bars are  $1\sigma$ . The mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio is effectively set at accretion. On the other hand, the  $^{21}\text{Ne}/^{22}\text{Ne}$  evolves as a function of the degree of degassing of a mantle reservoir with low ratios indicating a less degassed reservoir. Because mantle-derived basalts have vesicles with variable degrees of air contamination, step crushing produces a linear array that lies between air and the mantle composition. Projecting the best fit line through the step crushes to the mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio value yields the mantle  $^{21}\text{Ne}/^{22}\text{Ne}$  ( $^{21}\text{Ne}/^{22}\text{Ne}_E$ ). While the MORB source has a  $^{20}\text{Ne}/^{22}\text{Ne}$  of 12.5 (Ballentine et al., 2005; Ballentine and Holland, 2008; Raquin et al., 2008), the Iceland and Kola plumes have higher  $^{20}\text{Ne}/^{22}\text{Ne}$ , close to the solar composition (Mukhopadhyay, 2012; Yokochi and Marty, 2004). We projected the best fit line through the step crushes to the OIB–MORB mixing line, which subsequently defines the mantle source  $^{21}\text{Ne}/^{22}\text{Ne}_E$  of the basalts. The OIB endmember is based on the least radiogenic measured  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio at Galapagos (Kurz et al., 2009) and the MORB composition is from  $^{21}\text{Ne}/^{22}\text{Ne}_E$  in depleted MORBs from the Equatorial Atlantic (Tucker et al., 2012). Best fit lines were calculated using  $x$  and  $y$  error weighted fits forced through the atmospheric composition. L2012 is the Ne isotopic data for NLD-13 and NLD-27 from Lupton et al. (2012) and these data are used in calculating the error-weighted best fit lines.



**Fig. 3.**  $^4\text{He}/^3\text{He}$  ratios in the Rochambeau Rift samples plotted against  $^{21}\text{Ne}/^{22}\text{Ne}_E$  ratios. All of the Rochambeau samples have lower  $^{21}\text{Ne}/^{22}\text{Ne}_E$  compared to the North Atlantic popping rock (21D43; Moreira et al., 1998) and to depleted MORBs from the Equatorial Atlantic (Tucker et al., 2012). The Rochambeau samples appear to show a similar trend to the five Samoan xenoliths from Savai and PPT seamount (Poreda and Farley, 1992), but have a higher  $^{21}\text{Ne}/^{22}\text{Ne}_E$  compared to basalts from the Samoan islands of Ofu and Tau (Jackson et al., 2009). The OIB endmember is based on the lowest measured  $^4\text{He}/^3\text{He}$  ratio at Baffin Island (Stuart et al., 2003) and the least nucleogenic  $^{21}\text{Ne}/^{22}\text{Ne}$  from Galapagos (Kurz et al., 2009). The depleted mantle composition was selected based on extrapolating the trend observed in MORBs from the equatorial Atlantic (Tucker et al., 2012) to a  $^4\text{He}/^3\text{He}$  ratio of 73,000, which corresponds to the He isotopic composition in the most depleted MORBs from the Garret fracture zone (see Mahoney et al., 1994, discussion in Graham et al., 2001).  $R = (^3\text{He}/^{22}\text{Ne})_{\text{MORB}} / (^3\text{He}/^{22}\text{Ne})_{\text{plume}}$ . For reference, the fields for Kola (Yokochi and Marty, 2004), Galapagos (Kurz et al., 2009), Iceland (Moreira et al., 2001; Mukhopadhyay, 2012; Trierloff et al., 2000), Loihi (Honda et al., 1993a; Valbracht et al., 1997), and Manus Basin (Shaw et al., 2001) are shown.

sources, we correct for shallow level atmosphere contamination through least-squares fitting of well-defined arrays in  $^{21}\text{Ne}/^{22}\text{Ne}$ – $^{20}\text{Ne}/^{22}\text{Ne}$ ,  $^{20}\text{Ne}/^{22}\text{Ne}$ – $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$ – $^{129}\text{Xe}/^{130}\text{Xe}$  spaces. The fits are then extrapolated to the mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio. Correction for air contamination is an error-weighted linear least-squares extrapolation for  $^{21}\text{Ne}/^{22}\text{Ne}$

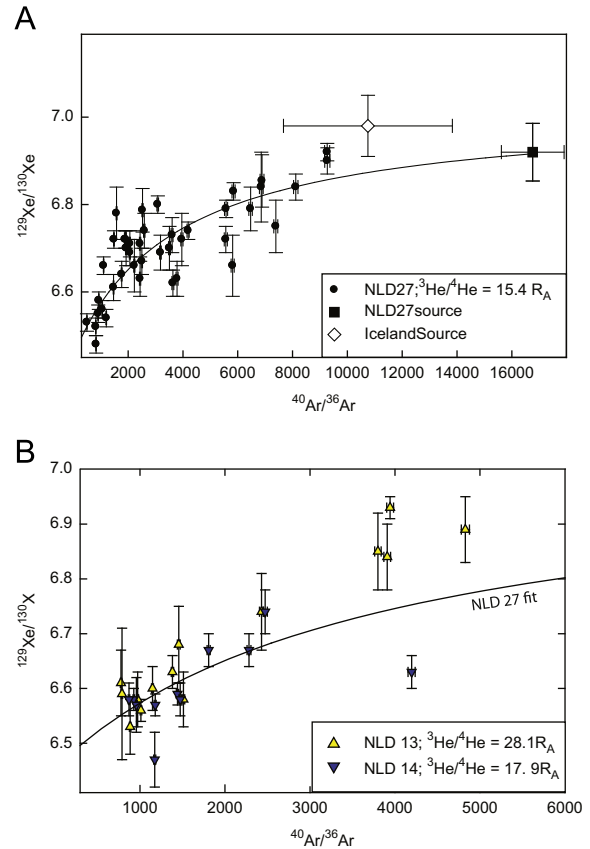


**Fig. 4.** (A) Ne–Ar compositions of individual step crushes for the NLD-27 sample from the Rochambeau Rift.  $^{40}\text{Ar}$  is generated by radioactive decay of  $^{40}\text{K}$  and low  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are indicative of a less degassed mantle. Popping rock from the North Mid-Atlantic Ridge is shown for comparison (Moreira et al., 1998) and the Bravo Dome well gas data is from Holland and Ballentine (2006). The vesicle compositions in basaltic glass are a combination of magmatic gases and shallow-level post-eruptive air contamination. Step crushing leads to sampling of vesicles with varying degrees of air contamination, which in Ne–Ar space should lead to a hyperbolic trend. A least-squares hyperbolic fit through the data indicate that the mantle source for NLD-27 (Rochambeau source) has a  $^{40}\text{Ar}/^{36}\text{Ar}$  of  $16,763 \pm 1144$  for a mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  of 13.22 (see text for discussion). (B) Step crushes from samples NLD-13 and NLD-14. The hyperbolic best fit regression for NLD-27 is overlain on the data. The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios for the NLD-13 and NLD-14 mantle sources may be comparable to that of NLD-27. Comparisons of the Ne–Ar isotopic compositions in individual step-crushes from RR with step-crushing data from other mantle plumes are in Supplemental Fig. 1.

(Figs. 2 and 3) and hyperbolic least-squares fits for mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios (Figs. 4 and 5).

While recent work based on continental well gas and the gas-rich popping rock from the north mid-Atlantic Ridge suggests that the MORB source has a  $^{20}\text{Ne}/^{22}\text{Ne}$  of 12.5 (Ballentine et al., 2005; Holland and Ballentine, 2006; Raquin et al., 2008), the Iceland (Mukhopadhyay, 2012) and Kola plumes (Yokochi and Marty, 2004) have a  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio closer to the solar wind value (13.8). Therefore, we used the least nucleogenic  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio from Galapagos (Kurz et al., 2009) and a solar  $^{20}\text{Ne}/^{22}\text{Ne}$  of 13.8 as the composition of the OIB end-member. The mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ( $^{21}\text{Ne}/^{22}\text{Ne}_E$ ) of the RR samples were determined by projecting the best fit line through the step crushes to the MORB–OIB end-member mixing line (Fig. 2). The mantle source  $^{20}\text{Ne}/^{22}\text{Ne}$  values are used to characterize the mantle source Ar and Xe isotopic compositions from the Ne–Ar and Ar–Xe hyperbolic fits (Figs. 4 and 5). We note that extrapolating Ar and Xe isotopic ratios to a mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  value of 12.5 would not affect our overall conclusions.

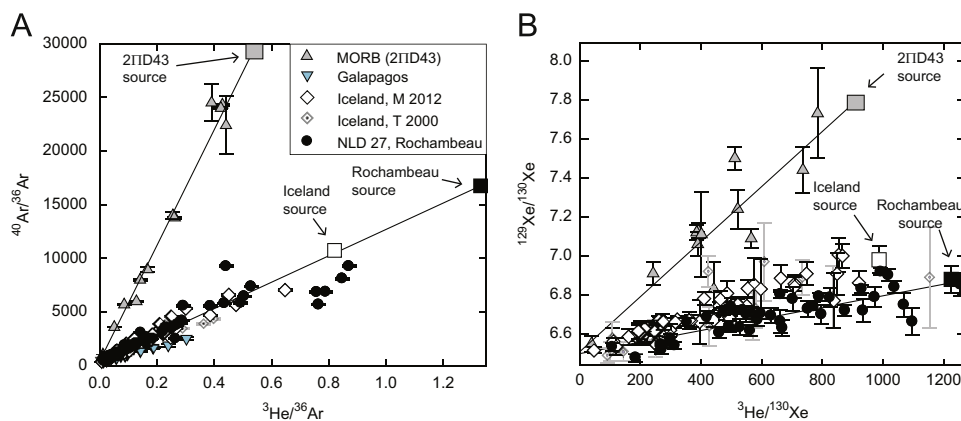
The  $x$  and  $y$  error-weighted linear least square fits (Mukhopadhyay, 2012) through the Ne data yield mantle  $^{21}\text{Ne}/^{22}\text{Ne}_E$  values between  $0.0423 \pm 0.0004$  and  $0.0480 \pm 0.0002$



**Fig. 5.** (A) Hyperbolic mixing between  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  for the NLD-27 sample from the Rochambeau Rift. Like for Ne–Ar, step crushing leads to sampling of vesicles with varying degrees of air contamination, which will generate a hyperbolic trend between the atmospheric composition and the mantle composition. The correlation shows scatter, likely reflecting the presence of a second elementally fractionated shallow-level air contaminant (also see Parai et al., 2012). A least squares hyperbolic best-fit curve through the data, when projected to a mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  of 13.22, yields a mantle source  $^{129}\text{Xe}/^{130}\text{Xe}$  value of  $6.92 \pm 0.07$ , significantly lower than measured values in MORBs but similar to the Iceland source of  $6.98 \pm 0.07$ . Note that given the curvature in Ar–Xe space, the defined  $^{129}\text{Xe}/^{130}\text{Xe}$  in the Rochambeau mantle source is not particularly sensitive to the exact choice of the mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio. (B) Step crushes showing the Ar–Xe relation for NLD-13 and NLD-14. The hyperbolic best fit regression for NLD-27 is overlain on the data.

(Fig. 2). Thus, all of the Rochambeau samples are less nucleogenic than the N. Mid-Atlantic Ridge popping rock ( $^{21}\text{Ne}/^{22}\text{Ne}_E = 0.0598 \pm 0.0003$ ; Moreira et al., 1998) and the depleted MORBs from the Equatorial Atlantic ( $0.0618 \pm 0.0003$ – $0.0648 \pm 0.0003$ ; Tucker et al., 2012).

To determine the mantle source Ar and Xe isotopic ratios, we only use sample NLD-27, for which a relatively large number of steps yield a well-defined hyperbola in Ne–Ar and Ar–Xe spaces (Figs. 4 and 5; Supplemental Tables 1 and 2). The extrapolated mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio ( $^{40}\text{Ar}/^{36}\text{Ar}_E$ ) for NLD 27 is  $16,763 \pm 1144$ , significantly lower than the estimated source values of  $27,000 \pm 4000$  for popping rock (Raquin et al., 2008),  $41,050 \pm 2670$  for the Bravo Dome well gas (Holland and Ballentine, 2006) and  $41,500 \pm 9000$  for the depleted Equatorial Atlantic MORBs (Tucker et al., 2012). The  $^{40}\text{Ar}/^{36}\text{Ar}_E$  for the Rochambeau sample is higher than the Iceland plume source  $^{40}\text{Ar}/^{36}\text{Ar}_E$  of  $10,732 \pm 3080$  (Mukhopadhyay, 2012). While we do not have sufficient number of step crushes for NLD-13 and NLD-14 to independently constrain the mantle source value for these two samples, the step crush data do in general fall on the hyperbolic best fit line for NLD-27 (Fig. 4). Hence, all three RR samples may have similar mantle  $^{40}\text{Ar}/^{36}\text{Ar}_E$  values.



**Fig. 6.** Elemental abundance ratios plotted against radiogenic isotope ratios for NLD-27 (Rochambeau Rift), DICE 10 (Iceland), Galapagos plume and popping rock (MORB). (A)  ${}^3\text{He}/{}^{36}\text{Ar}$  vs.  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  and (B)  ${}^3\text{He}/{}^{130}\text{Xe}$  vs.  ${}^{129}\text{Xe}/{}^{130}\text{Xe}$ . Iceland data is from Mukhopadhyay (2012); M 2012 and Trieloff et al. (2000); T 2000, the Galapagos data is from Raquin and Moreira (2009), and the popping rock (21D43) data is from Moreira et al. (1998). Good linear relationships are observed between isotope ratios and elemental ratios, which reflect mixing between mantle-derived noble gases and post-eruptive atmospheric contamination. Note that both the Rochambeau and Iceland plumes define the same trend but are quite distinct from popping rock (MORB source). The mixing lines denote the trajectory along which the mantle source will evolve towards the air composition as subducted air is mixed into the mantle source. Therefore, the low  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  and low  ${}^{129}\text{Xe}/{}^{130}\text{Xe}$  ratios in plumes cannot be generated by adding subducted air to a MORB-like mantle.

The hyperbolic fit for NLD-27 in Ar–Xe isotope space yields a mantle source  ${}^{129}\text{Xe}/{}^{130}\text{Xe}$  ( ${}^{129}\text{Xe}/{}^{130}\text{Xe}_E$ ) ratio of  $6.92 \pm 0.07$ , similar to the maximum measured  ${}^{129}\text{Xe}/{}^{130}\text{Xe}$  values at the RR and reported values of Samoan xenoliths (Fig. 5). The mantle source value for NLD-27 is significantly lower than source values of 7.6 for popping rock (Moreira et al., 1998),  $7.9 \pm 0.14$  for Bravo Dome (Holland and Ballentine, 2006) and  $7.77 \pm 0.06$  for depleted Equatorial Atlantic MORBs (Tucker et al., 2012). The composition of NLD-27, however, overlaps with the Iceland  ${}^{129}\text{Xe}/{}^{130}\text{Xe}_E$  ratio of  $6.98 \pm 0.07$  (Mukhopadhyay, 2012). For a given  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratio NLD-13 appears to have higher  ${}^{129}\text{Xe}/{}^{130}\text{Xe}$  ratios and thus, may have a higher mantle source value than NLD-27. However, additional data will be required to verify this claim. In any case, our observations confirm that the lower  ${}^{129}\text{Xe}/{}^{130}\text{Xe}$  ratios are not a result of shallow-level (syn- and post-eruptive) air contamination, but are a characteristic of the plume source.

#### 4. Relationships between elemental ratios and isotopic ratios

##### 4.1. Helium–Neon in the Rochambeau Rift source

The  ${}^4\text{He}/{}^3\text{He}$  and  ${}^{21}\text{Ne}/{}^{22}\text{Ne}_E$  isotopic compositions of the four Rochambeau samples show the influence of a mantle plume, and the He–Ne isotopic ratios can be explained by mixing between a less degassed mantle source (e.g., FOZO) and a depleted MORB source (Figs. 2 and 3). As shown in Fig. 3, for a given  ${}^4\text{He}/{}^3\text{He}$  ratio, the Rochambeau samples have a higher  ${}^{21}\text{Ne}/{}^{22}\text{Ne}_E$  compared to Iceland and Galapagos (Dixon et al., 2000; Moreira et al., 2001; Mukhopadhyay, 2012; Trieloff et al., 2000; Raquin and Moreira 2009; Kurz et al., 2009), but overlap with the range of compositions seen at Hawaii and Samoa (Honda et al., 1993a; Valbracht et al., 1997; Jackson et al., 2009; Poreda and Farley, 1992). The higher  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$  at a given  ${}^4\text{He}/{}^3\text{He}$  ratio reflects a higher  ${}^3\text{He}/{}^{22}\text{Ne}$  in the Rochambeau basalts compared to plume sources at Iceland and Galapagos. High  ${}^3\text{He}/{}^{22}\text{Ne}$  ratios in Rochambeau basalts have been previously observed and discussed in detail by Hahm et al. (2012) and Lupton et al. (2012). Here we summarize two possible explanations for the high  ${}^3\text{He}/{}^{22}\text{Ne}$  ratios:

- (i) The plume material that flows into the RR has a higher  ${}^3\text{He}/{}^{22}\text{Ne}$  ratio than the Iceland and Galapagos plumes. For

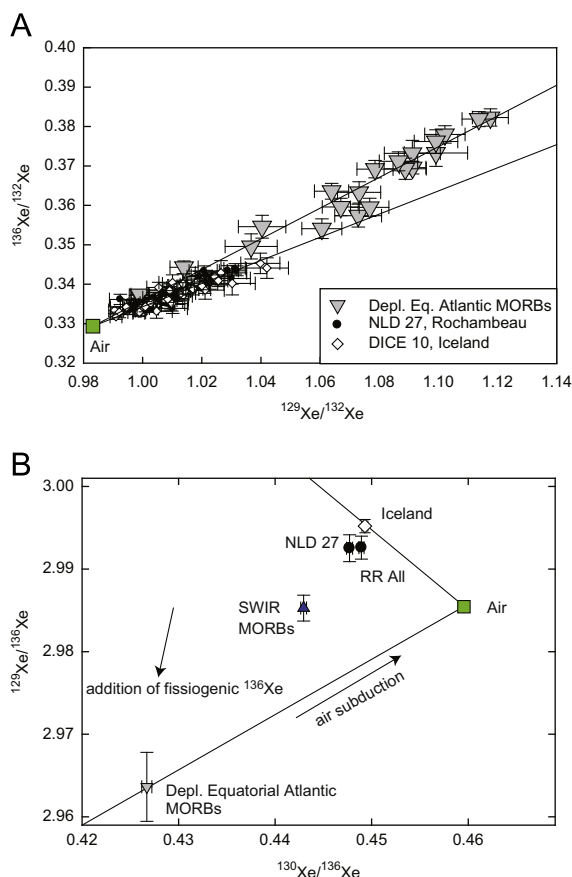
example, Yokochi and Marty (2004) have previously shown that mantle plumes may have different  ${}^3\text{He}/{}^{22}\text{Ne}$  ratios and in particular, the Kola plume has a significantly higher  ${}^3\text{He}/{}^{22}\text{Ne}$  ratio than Iceland and Galapagos.

- (ii) Mixing between melts derived from the plume and melts derived from the depleted back-arc mantle (see discussions in Hahm et al., 2012; Lupton et al., 2012). We note that high  ${}^3\text{He}/{}^{22}\text{Ne}$  ratios have also been observed in the Manus back-arc basin (Shaw et al., 2001). A higher  $\text{CO}_2$  content of the plume (Hahm et al., 2012) could lead to the plume melts undergoing more degassing than melts from the back-arc mantle (e.g., Gonnermann and Mukhopadhyay, 2007). Mixing of such degassed melts could produce the higher  ${}^{21}\text{Ne}/{}^{22}\text{Ne}$  at a given  ${}^4\text{He}/{}^3\text{He}$  ratio for the Rochambeau basalts compared to Iceland and Galapagos.

##### 4.2. Distinct mantle sources inferred from Helium–Argon relationships

The most gas rich sample in our study, NLD-27, has a  ${}^4\text{He}/{}^{40}\text{Ar}^*$  ratio of 3.3 (where  ${}^*$  indicates radiogenic), which is within the range of estimated mantle production ratios (1.6–4.2; e.g., Graham, 2002). Hence, NLD-27 preserves relatively unfractionated mantle noble gas elemental ratios, and we focus on this sample for the rest of the manuscript. Additionally, this is the only sample with well constrained mantle source  ${}^{40}\text{Ar}/{}^{36}\text{Ar}_E$  and  ${}^{129}\text{Xe}/{}^{130}\text{Xe}_E$  ratios and we assume that the sample is representative of the heavy noble gas characteristics of the plume source at Rochambeau. There are, however, clear variations in Ne and He isotopic compositions at Rochambeau, which suggests that the Ar and Xe isotopic composition of the RR basalts may not be homogeneous. Nonetheless, our goal is to investigate differences in heavy noble gas compositions between MORBs and plumes even in a plume-derived sample without the most primitive isotopic composition.

The step crushes from NLD-27 demonstrate an excellent correlation between  ${}^3\text{He}/{}^{36}\text{Ar}$  and  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratios (Fig. 6a). The  ${}^3\text{He}/{}^{36}\text{Ar}$  ratio of 1.33 for the NLD-27 source is higher than both the popping rock and Bravo Dome well gas sources, which have values of 0.4 and 0.3, respectively (Holland and Ballentine, 2006; Moreira et al., 1998). The  ${}^3\text{He}/{}^{36}\text{Ar}$  ratio of the mantle can decrease over time because of preferential recycling of atmospheric Ar (Fig. 6a). Thus, the higher  ${}^3\text{He}/{}^{36}\text{Ar}$  in Iceland and



**Fig. 7.** (A) Differences in measured  $^{129}\text{Xe}/^{132}\text{Xe}$ – $^{136}\text{Xe}/^{132}\text{Xe}$  between plumes (Iceland and Rochambeau) and depleted MORBs (equatorial Atlantic; Tucker et al., 2012). Step crushes in MORBs define a slope of  $0.3898 \pm 0.0081$  (MSWD=0.78) while the plume data define a slope of  $0.2937 \pm 0.0065$  (MSWD=0.68). Thus, the depleted MORBs and the Rochambeau and Iceland plumes sources have clear differences in the proportion of radiogenic to fissiogenic Xe; the MORB and plume sources cannot be related to each other solely through recycling of atmospheric Xe. (B) Error weighted averages of measured  $^{129}\text{Xe}/^{136}\text{Xe}$  and  $^{130}\text{Xe}/^{136}\text{Xe}$  isotope ratios from Iceland and Rochambeau plumes, MORBs from the Southwest Indian Ridge ( $n=104$ ; Parai et al., 2012) and depleted MORBs from the Equatorial Atlantic ( $n=25$ ; Tucker et al., 2012). RR ALL stands for the error-weighted average derived from all the step crushes on the NLD-13, NLD-14 and NLD-27 ( $n=67$ ; Supplemental Table 2). The measured values have not been corrected for post-eruptive air contamination. However, both post-eruptive contamination and recycling of atmospheric Xe will move the mantle source composition linearly towards the atmospheric composition. Therefore, the small Xe isotopic difference between the Rochambeau–Iceland plumes and MORBs cannot be related solely through recycling atmospheric Xe or by adding fissiogenic  $^{136}\text{Xe}$  to MORB Xe.

Rochambeau plumes cannot be related to recycling of atmospheric noble gases into a MORB-like mantle source (Fig. 6a). Likewise, the lower  $^{40}\text{Ar}/^{36}\text{Ar}_E$  ratio of plumes cannot be explained solely through recycling of air into the MORB source (Fig. 6a), suggesting a less degassed source is required to explain the low  $^{40}\text{Ar}/^{36}\text{Ar}_E$  ratios of plumes.

The Iceland, Galapagos, and Rochambeau samples define very similar slopes in  $^3\text{He}/^{36}\text{Ar}$ – $^{40}\text{Ar}/^{36}\text{Ar}$  space, even though the Rochambeau basalt has a higher  $^3\text{He}/^{22}\text{Ne}$ . Thus, the higher  $^3\text{He}/^{22}\text{Ne}$  ratio at Rochambeau probably reflects depletion in Ne rather than an enrichment of He. While the Ne–Ar measurements from Galapagos (Raquin and Moreira, 2009) do not yet constrain the mantle  $^{40}\text{Ar}/^{36}\text{Ar}_E$  at Galapagos (see Supplemental Fig. 1), the Iceland source has lower  $^{40}\text{Ar}/^{36}\text{Ar}_E$  and, hence, lower  $^3\text{He}/^{36}\text{Ar}$  ratios than the Rochambeau source. The Iceland source composition could be related to the Rochambeau source through a greater proportion of recycled Ar. Hence, the He–Ar results suggest both

recycling of atmospheric Ar and the existence of a less degassed component in the plume source.

#### 4.3. Ancient MORB–OIB separation inferred from Helium–Xenon relationships

The  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios from the individual step crushes on NLD-27 also show an excellent correlation with the  $^3\text{He}/^{130}\text{Xe}$  ratios (Fig. 6b).  $^3\text{He}$  and  $^{130}\text{Xe}$  are primordial isotopes, while  $^{129}\text{Xe}$  is produced from decay of extinct  $^{129}\text{I}$  (half-life=15.7 Myr).

The data displayed in Fig. 6b demonstrate that compared to the MORB source, the Rochambeau and Iceland mantle sources evolved with different I/Xe ratios. The step crushes from the NLD-27 sample display a slope that is quite distinct from the gas-rich MORB 21D43 (popping rock), but is similar to the correlation defined by Iceland. Since mixing of mantle with atmospheric noble gases in  $^3\text{He}/^{130}\text{Xe}$ – $^{129}\text{Xe}/^{130}\text{Xe}$  space is linear, adding subducted atmospheric Xe to the MORB-source will move the source composition towards air along a straight line (Fig. 6b). Hence, recycling of atmospheric Xe to the MORB source cannot produce the Rochambeau and Iceland mantle source compositions (Fig. 6b). Similarly, plume sources with similar composition to Rochambeau and Iceland cannot supply Xe to the MORB source, unless radiogenic  $^{129}\text{Xe}$  is added to MORBs. However,  $^{129}\text{I}$  became extinct at  $\sim 4.45$  Ga. As a result, the difference in MORB and plume  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios must have been set up early and the last major equilibration between the two reservoirs must predate 4.45 Ga as otherwise the differences in  $^{129}\text{Xe}/^{130}\text{Xe}$  would not be preserved in the present-day mantle.

#### 5. Preservation of long-term heterogeneities in the mantle inferred from xenon isotopes

The Xe isotopic compositions of mantle-derived rocks provide information about early degassing and mantle differentiation. In addition to  $^{129}\text{Xe}$  that was produced from decay of extinct  $^{129}\text{I}$ ,  $^{136}\text{Xe}$  was produced by spontaneous fission of now extinct  $^{244}\text{Pu}$  (half-life=80 Myr). However,  $^{136}\text{Xe}$  is also generated by spontaneous fission of extant  $^{238}\text{U}$ . Thus, the I–Xe and Pu–Xe systems are sensitive to the first  $\sim 100$  Myr and 500 Myr of the Solar System, respectively, while the U–Xe system evolves throughout Earth history.

The error-weighted mean xenon isotope composition ( $^{129}\text{Xe}/^{136}\text{Xe}$  vs.  $^{130}\text{Xe}/^{136}\text{Xe}$ ) of NLD-27, of all four of the Rochambeau samples, Iceland (Mukhopadhyay, 2012), MORBs from the Southwest Indian Ridge (Parai et al., 2012) and MORBs from the Equatorial Atlantic (Tucker et al., 2012) are shown in Fig. 7. Our observations demonstrate that MORBs and plumes have small but distinct differences in  $^{129}\text{Xe}/^{136}\text{Xe}$  ratios. Because all of the plotted samples were analyzed using the same procedure in the same laboratory, the differences between these groups of basalts cannot be related to inter-laboratory artifacts. We note that the data plotted in Fig. 7 have not been corrected for post-eruptive air contamination, so the mantle source compositions will lie further from the atmospheric composition along the straight line joining the measured and atmospheric compositions. However, correcting for shallow-level air contamination is not required to demonstrate that the Rochambeau (and Iceland) source cannot be related to the MORB source by addition of atmospheric xenon. Thus, while recycling of atmospheric Xe may occur to the deep Earth (Holland and Ballentine, 2006; Kendrick et al., 2011; Mukhopadhyay, 2012; Tucker et al., 2012), we emphasize that recycling by itself cannot explain the difference in  $^{129}\text{Xe}/^{136}\text{Xe}$  ratio between MORBs and plumes. Likewise, mixing MORB Xe with fissiogenic  $^{136}\text{Xe}$  in recycled slabs will lead

to a decrease in the  $^{129}\text{Xe}/^{136}\text{Xe}$  ratio. Hence, plume Xe cannot be a mixture of MORB and fissiogenic Xe.

The  $^{129}\text{Xe}/^{136}\text{Xe}$  ratio is a measure of the time integrated  $^{129}\text{I}/(^{244}\text{Pu} + ^{238}\text{U})$  ratio and the differences in the Xe isotopic composition between the different basalt groups (Fig. 7) can be explained by mantle processing and mixing of less degassed and more degassed mantle sources. A mantle reservoir that undergoes degassing after I and Pu are extinct will have low concentrations of primordial  $^{130}\text{Xe}$ , radiogenic  $^{129}\text{Xe}$  and fissiogenic  $^{136}\text{Xe}$  produced by extinct  $^{244}\text{Pu}$ . Addition of  $^{136}\text{Xe}$  from  $^{238}\text{U}$  fission to such a degassed source would decrease both the  $^{129}\text{Xe}/^{136}\text{Xe}$  and the  $^{130}\text{Xe}/^{136}\text{Xe}$  ratios of the reservoir (Fig. 7b). Hence, the plume sources are less degassed than the MORB source, a conclusion that is based only on the Xe isotopic ratios and independent of the absolute concentration of noble gases or the partitioning of noble gases with respect to their radiogenic parents.

### 5.1. Pu–U–I systematics in the Rochambeau Rift source

The  $^{244}\text{Pu}$ - and  $^{238}\text{U}$ -produced fission isotopes of Xe ( $^{131,132,134,136}\text{Xe}$ ) provide information about mantle processing rates, particularly during the Hadean (e.g., Allègre et al., 1987; Coltice et al., 2009; Kunz et al., 1998; Ozima et al., 1985; Yokochi and Marty, 2005).  $^{244}\text{Pu}$  and  $^{238}\text{U}$  produce the four fission isotopes in different proportions and fission Xe yields from Pu are significantly larger than from U. A reservoir that has remained completely closed to volatile loss over Earth's history will have  $^{136}\text{Xe}_{\text{Pu}}^*/^{136}\text{Xe}_{\text{U}}^*$  of  $\sim 27$ , where  $^*$  refers to fissiogenic Xe (Tolstikhin et al., 2006; Tolstikhin and O'Nions, 1996).  $^{244}\text{Pu}$  became extinct at  $\sim 4$  Ga and reservoirs that underwent extensive degassing over the past 4 Ga would have lost a significant fraction of the Pu-produced fission Xe and, thus, have a large proportion of  $^{238}\text{U}$ -derived fission Xe; i.e.,  $^{136}\text{Xe}_{\text{Pu}}^*/^{136}\text{Xe}_{\text{U}}^*$  in degassed reservoirs will be  $\ll 27$ . Consequently, deconvolving  $^{244}\text{Pu}$ - from  $^{238}\text{U}$ -produced fission Xe using the measured isotopic ratios provides a direct constraint on the degree of outgassing of a mantle reservoir.

To deconvolve  $^{238}\text{U}$ - from  $^{244}\text{Pu}$ -derived fissiogenic Xe, five Xe isotopes were used ( $^{130,131,132,134,136}\text{Xe}$ ). A sufficient number of step-crushes are available for NLD-27 and deconvolution of Pu- from U-derived Xe was performed for only this sample. In mantle-derived basalts, different vesicles have different proportions of mantle Xe and post-eruptive atmospheric Xe contamination. To

determine the mantle source fission isotopic compositions, the  $^{129}\text{Xe}/^{132}\text{Xe}$  ratios in the individual steps were first regressed against the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio using a least squares hyperbolic fit, which yielded a mantle source  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio of  $1.038 \pm 0.006$  (Supplemental Fig. 2). Next, the  $^{130,131,134,136}\text{Xe}/^{132}\text{Xe}$  ratios obtained from the step-crushes were regressed against the  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio. From the slopes and uncertainties in the slopes, the mantle  $^{130,131,134,136}\text{Xe}/^{132}\text{Xe}$  ratios, along with their uncertainties, were calculated for the mantle  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio of 1.038 (Supplemental Table 3). To investigate whether inclusion of some of the less precise measurements affect the fission deconvolution, the above analyses were redone using a filtered data set; only data points with  $^{132}\text{Xe}/^{136}\text{Xe}$  distinct from the atmospheric composition at the  $2\sigma$  level and with a relative error of  $< 1\%$  were selected. Such filtering only eliminates 4 data points and does not affect the deconvolution.

Following determination of the mantle source composition, the least-squares solution to the system  $A \cdot x = b$  was found with the following additional constraints:  $\sum x_i = 1$  and  $0 \leq x_i \leq 1$  (also see Caffee et al., 1999; Mukhopadhyay, 2012). Here,  $A$  defines the composition matrix of the end-members,  $x$  is the vector defining the fraction of each component, and  $b$  is the sample composition vector. End-member and mantle source compositions ( $A$  and  $b$ , respectively) were normalized to the standard deviations in the mantle source isotope ratios to assign equal weight to each isotope ratio. To compute the uncertainties, a Monte Carlo technique was used whereby the estimated sample composition was varied at random within the  $1\sigma$  uncertainty and the least squares fit recomputed using the new values. For all simulations, it was verified that convergence to a minimum was achieved.

For the initial Xe isotopic composition of the mantle, we investigated chondritic (AVCC) and solar Xe. We selected AVCC and solar Xe based on (i) recent observations of AVCC Kr in the mantle (Holland et al., 2009), (ii)  $^{128}\text{Xe}/^{130}\text{Xe}$  excess with respect to air in continental well gases (Caffee et al., 1999; Holland et al., 2009) and (iii) lower extent of Xe mass fractionation in the Archean atmosphere compared to the present day atmosphere (Pujol et al., 2011). The initial mantle compositions along with the isotopic compositions of Pu- and U-produced fission Xe used for the deconvolution are listed in Supplemental Table 3.

Depending on whether the initial mantle Xe is solar or chondritic, the fraction of  $^{136}\text{Xe}$  derived from  $^{244}\text{Pu}$  fission is  $0.89^{+0.11}_{-0.14}$  or  $0.88^{+0.11}_{-0.20}$ , respectively (Table 1). The Pu-

**Table 1**

Fission Xe deconvolution for the NLD 27 source (Rochambeau) compared to sources for DICE 10 (Iceland), and equatorial Atlantic MORBs.

Starting mantle composition	Sample	Fraction $^{132}\text{Xe}$ from recycled air	Fraction $^{132}\text{Xe}$ from AVCC/SW	Fraction $^{132}\text{Xe}$ from $^{238}\text{U}$	Fraction $^{132}\text{Xe}$ from $^{244}\text{Pu}$	Fraction $^{136}\text{Xe}$ from $^{244}\text{Pu}$	$^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$
AVCC	NLD-27	0.888	0.093	0.020	0.0176	$0.88^{+0.11}_{-0.20}$	$3.2^{+1.2}_{-0.4}$
	Rochambeau	$\pm 0.023$	$\pm 0.022$	$\pm 0.020$	$\pm 0.0035$		
	Iceland-2 <sup>a</sup>	0.924	0.056	0.001	0.0189	$0.91^{+0.09}_{-0.15}$	$3^{+0.1}_{-0.2}$
		$\pm 0.024$	$\pm 0.022$	$\pm 0.001$	$\pm 0.0034$		
	MORBs <sup>b</sup> (Eq. Atlantic)	0.910	0.046	0.028	0.017	$0.25^{+0.17}_{-0.10}$	$10.7^{+7.4}_{-4.6}$
	$\pm 0.052$	$\pm 0.049$	$\pm 0.005$	$\pm 0.008$			
Solar Wind	NLD-27	0.864	0.1132	0.0019	0.0212	$0.89^{+0.11}_{-0.14}$	$2.9^{+0.6}_{-0.4}$
	Rochambeau	$\pm 0.023$	$\pm 0.021$	$\pm 0.0017$	$\pm 0.0035$		
	Iceland-2 <sup>a</sup>	0.959	$0.024^{+0.026}_{-0.024}$	0.005	0.014	$0.66 \pm 0.19$	$4.8^{+1.4}_{-1.8}$
		$\pm 0.04$		$\pm 0.0026$	$\pm 0.005$		
	MORBs <sup>b</sup> (Eq. Atlantic)	0.896	0.058	0.027	0.019	$0.29^{+0.14}_{-0.12}$	$8.9^{+6.5}_{-3.1}$
	$\pm 0.054$	$\pm 0.049$	$\pm 0.004$	$\pm 0.008$			

$^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  is the ratio of radiogenic  $^{129}\text{Xe}$  from decay of  $^{129}\text{I}$  to fissiogenic  $^{136}\text{Xe}$  derived from  $^{244}\text{Pu}$  fission. The distributions of  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  are skewed and hence, the medians and the 67% confidence intervals are presented.

<sup>a</sup> Deconvolutions are presented in Mukhopadhyay (2012).

<sup>b</sup> Deconvolutions are presented in Tucker et al. (2012).

derived  $^{136}\text{Xe}$  fractions are similar to those from the Iceland plume (Mukhopadhyay, 2012; Table 1), but higher than values of 0.30–0.60 inferred for the Kola plume (Yokochi and Marty, 2005). The values for the Kola plume were inferred from correlations between  $^{21}\text{Ne}/^4\text{He}$  and  $^{136}\text{Xe}/^4\text{He}$ . The lower values at Kola may arise for multiple reasons: (i) elemental ratios can be fractionated through a combination of solubility- and diffusivity-controlled degassing (Gonnermann and Mukhopadhyay, 2007; Paonita and Martelli, 2007; Yokochi and Marty, 2005); (ii) the  $^4\text{He}/^{21}\text{Ne}$  production ratio could be different from the value of  $2.22 \times 10^7$  (Yatsevich and Honda, 1997) used by Yokochi and Marty (2005) (see Leya and Wieler, 1999; Hünemohr, 1989); and/or (iii) plumes may have different proportions of Pu-derived Xe depending upon the ratio of recycled to primitive material.

The Iceland and Rochambeau plume values, however, are clearly higher than values of  $0.25^{+0.17}_{-0.1}$ – $0.29^{+0.14}_{-0.12}$  for the depleted MORB source (Tucker et al., 2012; Table 1). Since the Iceland, Rochambeau and depleted MORB data were obtained in the same laboratory using the same techniques, the higher proportion of  $^{244}\text{Pu}$ -derived  $^{136}\text{Xe}$  in plumes is a robust result. A higher fraction of  $^{244}\text{Pu}$ -derived  $^{136}\text{Xe}$  is a clear indicator of a less degassed source, and hence, we conclude that the Rochambeau and Iceland plume sources must sample a less degassed mantle than the MORB source.

The combined I–Pu–Xe system can constrain the closure time for volatile loss of a mantle reservoir through the  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  ratio, where  $^*$  represents the radiogenic and fissionogenic decay products (Allègre et al., 1987; Azbel and Tolstikhin, 1993; Coltice et al., 2009; Kunz et al., 1998; Ozima et al., 1985; Pepin and Porcelli, 2006; Staudacher and Allègre, 1982; Yokochi and Marty, 2005). Since  $^{129}\text{I}$  has a shorter half-life than  $^{244}\text{Pu}$ , higher  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  ratios are indicative of earlier closure to volatile loss. We find that at Rochambeau the  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  ratio is  $2.9^{+0.6}_{-0.4}$  to  $3.2^{+1.2}_{-0.4}$  (Supplemental Table 2). While detailed modeling of the fission and radiogenic Xe isotopes is beyond the scope of this paper, we note that the  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  values at Rochambeau are comparable to those from Iceland but significantly lower than the MORB source (Table 1). Interpreting these values as closure ages for a mantle with an initially homogeneous I/Pu ratio, the higher  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  ratio in the depleted MORB source would imply that the shallow upper mantle became closed to volatile loss prior to the deep mantle reservoir supplying noble gases to the mantle plumes. Such a conclusion appears paradoxical. Rather, a simpler explanation is that the lower  $^{129}\text{Xe}^*/^{136}\text{Xe}_{\text{Pu}}^*$  in the Rochambeau and Iceland sources reflects a lower initial I/Pu ratio for the plume source compared to the MORB source. This difference would suggest that the initial phase of Earth's accretion was volatile poor compared to the later stages of accretion because Pu is a refractory element while I is a volatile element (e.g., Mukhopadhyay, 2012). Since this difference in I/Pu ratio is still preserved in the present day Xe isotopic ratio of the mantle, we argue that the whole mantle was never completely homogenized.

## 6. Implications for the age of mantle heterogeneities and mantle evolution

Our fundamental observations from Iceland and Rochambeau are that plumes have lower  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio and a higher proportion of Pu-derived fissionogenic Xe than MORBs, and the differences cannot be attributed solely to recycling of atmospheric noble gases. These observations require that the reservoirs supplying noble gases to plumes and MORBs were processed and outgassed to different extents within the first 100 Myr of Earth's history and that subsequently these reservoirs have not been homogenized. Models that

seek to explain the geochemical evolution of the mantle must satisfy this fundamental constraint from Xe isotopes.

We now discuss the constraints Xe isotopes place on mantle reservoirs and in particular evaluate whether our observations are consistent with two classes of models put forth to explain the geochemical evolution of the mantle: (i) the steady-state mantle models (e.g., Porcelli and Wasserburg, 1995; Tolstikhin and O'Nions, 1996; Tolstikhin et al., 2006) and (ii) models that generate reservoirs with primitive He isotopic signatures over Earth's history (e.g., Davies, 2010; Lee et al., 2010).

### 6.1. Steady-state mantle models

The differences in noble gas compositions between MORBs and OIBs are often interpreted in terms of steady-state mantle models that require primordial  $^3\text{He}$ ,  $^{22}\text{Ne}$ ,  $^{36}\text{Ar}$  and  $^{130}\text{Xe}$  and radiogenic  $^{129}\text{Xe}$  in the volatile-depleted MORB source to be derived from a more primitive volatile-rich plume source (Kellogg and Wasserburg, 1990; Porcelli and Wasserburg, 1995; Tolstikhin and O'Nions, 1996). Mixtures of the plume-derived noble gases, radiogenic noble gases produced in the MORB source, and subducted atmospheric Ar and Xe into the MORB source leads to the more radiogenic noble gas isotopic compositions observed in MORBs. While originally the plume source was assumed to be the whole lower mantle, the basic framework of the steady-state models could still be viable if instead of the whole lower mantle, the plume source was much smaller, such as  $D'$  (e.g., Tolstikhin et al., 2006).

If the primordial gases in the MORB source are derived from the plume source, then the ratios of primordial noble gases are expected to be the same in the two sources. However, OIBs and MORBs appear to have different  $^3\text{He}/^{22}\text{Ne}$ ,  $^3\text{He}/^{36}\text{Ar}$  and  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios (Honda and McDougall, 1998; Yokochi and Marty, 2004; Mukhopadhyay, 2012). Our Rochambeau data also show differences from MORBs. For example, the  $^3\text{He}/^{36}\text{Ar}$  is 1.3 in Rochambeau Rift source vs. 0.3 in the Bravo Dome well gas source (Holland and Ballentine, 2006). More importantly, in the steady-state models,  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio in the plume source is at least as high as in the MORB source, a prediction that is clearly refuted by our observations of lower  $^{129}\text{Xe}/^{130}\text{Xe}$  in the plume source. As noted earlier, the lower  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio in the plume source cannot arise solely from recycling. Thus, we suggest that all of the primordial gases and the radiogenic  $^{129}\text{Xe}$  in the MORB source cannot be derived from the plume source. Therefore, the two reservoir steady-state mantle models are not consistent with the observations and need to be re-evaluated.

### 6.2. Generation of a 'primordial-like' reservoir over time

In contrast to many models that assign the low  $^4\text{He}/^3\text{He}$  ratios observed in many OIBs to a primordial reservoir, Lee et al. (2010) suggested that a 'primordial-like' reservoir could have been produced during the first billion years of Earth's history through a process termed upside-down differentiation. A hotter mantle during the Hadean and earliest Archean led to partial melting at depths between 660 and 410 km, which produced Fe-rich melts (Lee et al., 2010). At these depths, the Fe-rich melts are denser than the surrounding mantle and sink to the core–mantle boundary, possibly forming the two large low shear wave velocity provinces at the base of the mantle. Since the melts never degas, they are volatile-rich, and because partial melting transfers the incompatible elements to the melts without fractionation, the melts have primordial time-integrated  $\text{U}/^3\text{He}$ ,  $\text{U}/^{204}\text{Pb}$ ,  $^{87}\text{Rb}/^{86}\text{Sr}$  and  $^{147}\text{Sm}/^{144}\text{Nd}$  today, i.e., a 'primordial-looking' reservoir (Lee et al., 2010). As the noble gases are highly incompatible (e.g., Heber et al., 2007), the model predicts that the primordial noble



gas elemental ratios (e.g.,  $^3\text{He}/^{22}\text{Ne}$ ,  $^3\text{He}/^{36}\text{Ar}$ ) of the melts would be the same as the solid convecting mantle. Importantly, differences in  $^{129}\text{Xe}/^{130}\text{Xe}$  between the MORB source and the low  $^4\text{He}/^3\text{He}$  reservoir are not expected, since the process of generating the 'primordial' reservoir occurs over for 1 Ga, well past the 100 Myr lifetime of  $^{129}\text{I}$ .

MORBs and low  $^4\text{He}/^3\text{He}$  OIBs, however, have different  $^3\text{He}/^{22}\text{Ne}$  (Honda and McDougall, 1998; Yokochi and Marty, 2004; Mukhopadhyay, 2012) and  $^3\text{He}/^{36}\text{Ar}$  ratios (Fig. 6; also see Mukhopadhyay, 2012). Most importantly, the  $^{129}\text{Xe}/^{130}\text{Xe}$  data contradict the hypothesis that the primitive looking noble gas reservoir could be generated by melt segregation to the CMB over timescales of 1 Ga. If the noble gases are from a reservoir that was produced after 4.45 Ga, plumes and MORBs would have the same  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio, or have  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios that can be related to each other through addition of subducted air. Thus, we rule out the upside-down differentiation as the main mechanism for producing a reservoir with primitive noble gas signatures. We stress that we do not argue against the generation of Fe-rich melts during the Hadean and early Archean (Lee et al., 2010), but argue that such a process by itself cannot generate the primitive noble gas signature seen in OIBs.

Davies (2010) suggested a somewhat similar hypothesis to Lee et al. (2010) to explain the primitive noble gas signatures of OIBs with two important distinctions: the process of generating the primitive-like noble gas reservoir occurs throughout Earth's history, and the process occurs under mid-ocean ridges in the shallow upper mantle when undegassed melts react with the peridotites to produce pyroxenites. The pyroxenites, being denser than the peridotites, sink to the deep mantle and are sequestered for long periods of time in the D' region. Consequently, the D' region acquires a more primitive noble gas signature than the MORB source that is continually depleted of volatiles. However, the noble gas characteristics for D' implied by Davies' (2010) model are the same as the upside-down differentiation model (Lee et al., 2010) discussed above. Hence, the same arguments presented above allow us to rule out Davies' (2010) hypothesis as the primary mechanism for generating the primitive noble gas signature of OIBs.

Several studies have suggested that low  $^4\text{He}/^3\text{He}$  ratios in OIBs are associated with depleted residues of mantle melting because U might be more incompatible than He (e.g., Coltice and Ricard, 1999; Parman, 2007). In such scenarios,  $^4\text{He}/^3\text{He}$  ratios similar to that observed in present-day OIBs could have been frozen in the U-depleted mantle residues that formed between 1–3 Ga and, thus, would not require the separation of the MORB and low  $^4\text{He}/^3\text{He}$  reservoirs over Earth's history. However, if low  $^4\text{He}/^3\text{He}$  ratios in OIBs are indeed due to sampling of a residual depleted mantle, then our  $^{129}\text{Xe}/^{130}\text{Xe}$  data from Iceland and Rochambeau require these residues to be generated prior to 4.45 Ga. Hence, long-term separation of the low  $^4\text{He}/^3\text{He}$  reservoir is still required.

### 6.3. The nature of the large low shear wave velocity provinces (LLSVPs)

Recent studies have suggested that plumes might originate from the LLSVPs at the base of the mantle (e.g., Burke, 2008; Dziewonski et al., 2010; Torsvik et al., 2006). Both primitive (Deschamps et al., 2011; Jackson and Carlson, 2011; Mukhopadhyay, 2012; Tolstikhin and Hofmann, 2005) and recycled material (Hutko et al., 2006; Tackley, 2011; Tan and Gurnis, 2005) have been invoked for LLSVPs. If plumes are indeed drawing material from LLSVPs, then based on the Iceland and Rochambeau Xe data we can conclusively say that these features must have been produced prior to 4.45 Ga (Figs. 6 and 7). Therefore, LLSVPs are long lasting structures in the deep mantle and are essentially as old as the age of the Earth.

Observed high proportions of Pu-derived fission Xe and recycled atmospheric Xe in both the Rochambeau and Iceland plume sources require that plumes sample both primitive and

recycled material. We note that the DICE 10 sample from Iceland has amongst the most primitive  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio, yet ~90% of its Xe is from a recycled source (Table 1). Hence, if all of the plume material is derived from LLSVPs, then these features must also be composed of both recycled and primitive lithologies. Alternatively, deep mantle flow could channel subducted slabs towards the margins of the LLSVPs, where they get entrained by the rising plumes. In this regard, we urge caution in using the measured lithophile isotopic compositions in low  $^4\text{He}/^3\text{He}$  ratio plume basalts as a direct measure of the composition of primitive mantle (Jackson et al., 2010).

## 7. Conclusions

We measured He, Ne, Ar, and Xe abundances and isotopic compositions of four basalts with low  $^4\text{He}/^3\text{He}$  ratios from the Rochambeau Rift in the northern Lau Back-arc Basin that are thought to be influenced by the Samoan plume. We documented that sample NLD-13 with a  $^4\text{He}/^3\text{He}$  ratio of 25,600 ( $28.1R_A$ ) has a  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of at least 4828 and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio of at least  $6.93 \pm 0.03$ . For NLD-27, for which we had a sufficient number of step crushes, we inferred a mantle source  $^{40}\text{Ar}/^{36}\text{Ar}_E$  ratio of  $16,763 \pm 1144$  and a  $^{129}\text{Xe}/^{130}\text{Xe}_E$  ratio of  $6.92 \pm 0.07$ .

The Xe isotopic results from the Lau Basin and Iceland indicate that the plume source has a low  $^{129}\text{Xe}/^{130}\text{Xe}_E$  that cannot result solely from adding subducted atmospheric Xe to MORB Xe. Rather, the plume source is less degassed and appears to have a lower I/Pu ratio compared to the MORB source. Our new observations are not consistent with steady-state mantle models or with the generation of primordial-looking reservoirs over Earth history (e.g., Lee et al., 2010; Davies, 2010; Coltice and Ricard, 1999). Rather, given the short half-life of  $^{129}\text{I}$ , the difference in  $^{129}\text{Xe}/^{130}\text{Xe}$  requires the MORB source and the reservoir that supplies primordial noble gases to plumes to have been processed and outgassed to different extents within the first 100 Myr of Earth's history. Subsequent to this period, the two reservoirs could not have been homogenized, as otherwise the difference in  $^{129}\text{Xe}/^{130}\text{Xe}$  would not be preserved in the present-day mantle. Models that seek to explain the dynamical and chemical evolution of the mantle must be compatible with these results. For example, if plumes are indeed derived from LLSVPs, then the Xe data require LLSVPs to have existed since 4.45 Ga.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.epsl.2013.02.012>.

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