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

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Abstract

Heavy noble gases (Ne, Ar, Xe) can record long-lasting heterogeneities in the mantle because of the production of isotopes from extant (^{238}U, ^{40}K) and extinct (^{129}I and ^{244}Pu) radionuclides. However, the presence of ubiquitous atmospheric contamination, 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 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}He/^{3}He ratios down to 25,600 (^{3}He/^{4}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}Ne/^{22}Ne, ^{40}Ar/^{36}Ar, and ^{129}Xe/^{130}Xe) compared to the mantle source of mid-ocean ridge basalts (MORBs). Additionally, we observe differences in elemental abundance patterns between the Rochambeau source and the mantle source of MORBs as characterized by the gas-rich popping rock from the Mid-Atlantic Ridge. However, the ^{3}He/^{22}Ne ratio of the Rochambeau plume source is significantly higher than the Iceland and Galapagos plume sources, while the ^{3}He/^{36}Ar and ^{3}He/^{130}Xe ratios appear to be similar. The difference in ^{3}He/^{22}Ne between Rochambeau and the Galapagos and Iceland plume sources could reflect long lasting accretional heterogeneities in the deep mantle or some characteristic of the back-arc mantle source.

High-precision xenon isotopic measurements indicate that the lower ^{129}Xe/^{130}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 fissiogenic xenon isotopes demonstrate a

higher proportion of Pu-derived fission Xe in the Rochambeau source compared to the MORB source. Therefore, both I/Xe and Pu/Xe ratios are different between OIB and MORB mantle sources. Our observations require heterogeneous volatile accretion and a lower degree of processing for the mantle plume source compared to the MORB source. Since differences in $^{129}Xe/^{130}Xe$ ratios have to be produced while ^{129}I is still alive, OIB and MORB sources were degassed at different rates for the first 100 Ma 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 observations require the preservation of less-degassed, early-formed heterogeneities in the Earth's deep mantle throughout Earth's history.

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 exosphere. 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 $^{4}He/^{3}He$, $^{21}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ (e.g., Hanyu et al., 2001; Honda et al.., 1993; Mukhopadhyay 2012; Poreda and Farley, 1992; Raquin and Moreira, 2009; Trieloff et al., 2000; Trieloff et al., 2002; Yokochi and Marty, 2004). Likewise, lower ratios of radiogenic to non-radiogenic Xe isotopes ($^{129}Xe/^{130}Xe$) are found in Hawaii, Samoa, Iceland and Reunion (e.g., Mukhopadhyay 2012; Poreda and Farley, 1992; Trieloff et al., 2000; Trieloff et al., 2002). 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., Allegre et al., 1987; Graham, 2002; Gonnermann and Mukhopadhyay, 2009; Kurz et al., 1982; Kurz et al., 2009; Porcelli and

Wasserburg, 1995; Staudacher and Allegre, 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 $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ 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; Trieloff and Kunz, 2005).

If the low $^{129}Xe/^{130}Xe$ 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}I, which produces ^{129}Xe, became extinct 100 million years 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 $^{129}Xe/^{130}Xe$ ratios in OIBs are from recycling of atmospheric Xe, long-term separation of the two sources is not required and extensive mixing between the sources is allowed. Hence, addressing the origin of the low $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ 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. (in press) demonstrated that the lower $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ in the Iceland plume compared to depleted MORBs (Moreira et al., 1998; Tucker et al., in press) 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 $^{4}He/^{3}He$ ratios as low as

25,600 (28.1 R_A, where R_A is the $^3He/^4He$ ratio normalized to the atmospheric ratio of 1.39×10^{-6}).

The Rochambeau Rift 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 Pacific mantle (Smith et al., 2001). While slab rollback could induce the southward mantle flow in the Lau back-arc, a consequence of such flow would be introduction of Samoan plume material into the northern Lau back-arc region (Smith et al., 2001) through the tear in the Tonga slab beneath the Vitiaz lineament (Millen and Hamburger, 1998).

The flow of Samoan plume material into the northern Lau basin is consistent with observations of low $^4He/^3He$ ratios along the Rochambeau Rift that slowly increase to MORB-like values southwards (Poreda and Craig, 1992; Lupton et al., 2009; Turner and Hawkesworth, 1998). For example, $^4He/^3He$ ratios along the Rochambeau Rift are as low as 32,700- 25,600 (22-28.1 R_A; Hahm et al., 2012; Poreda and Craig, 1992; Lupton et al., 2009). These values are similar to the lowest $^4He/^3He$ ratio of 21,000 at the nearby Samoan plume (34.2 R_A, Jackson et al., 2007; Farley et al., 1992). $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ ratios of up to 11,988 ± 156 and 7.04 ± 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 Rochambeau Rift, non-atmospheric $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ ratios should be expected in these basalts. Thus, basaltic glasses from the Rochambeau Rift could be ideal for characterizing the heavy noble gas composition of a low $^4He/^3He$ mantle plume. In this study, we use our combined He-Ne-Ar-Xe measurements from basaltic glass samples with low $^4He/^3He$ ratios from

the Rochambeau Rift to constrain the mantle source Ne, Ar and Xe isotopic composition. We use the source composition from Rochambeau to investigate whether the lower $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ 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 models of the dynamical and chemical evolution of the mantle are consistent with our new observations.

2. Analytical Methods

We analyzed four basaltic glass samples from the Rochambeau Rift: NLD 13, NLD 14, NLD 20 and NLD 27 (Fig. 1). $^{4}He/^{3}He$ ratios were previously measured by Lupton et al (2009) and range between 25,600 and 46,700 (15.4 R_A to 28.1 R_A; Table 1). Reported He concentrations range from 3 to 23 $\times$ 10^{-6} cm^3 STP g^{-1}. Glass chunks were carefully selected to avoid phenocrysts. In order to remove surface alteration, glasses were leached in 2% nitric acid for 10 to 20 minutes, and then ultrasonically cleaned in distilled water and acetone. Single pieces of basaltic glass (3.2 to 6.8 grams) were baked under vacuum for 24 hours at 100ºC and were pumped for an additional 6 to 12 days. Samples were crushed under vacuum 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 $^{40}Ar/^{36}Ar$ ratio. The noble gases were then trapped on a cryogenic cold-finger. He was separated from Ne at 32 K and let into the Nu Noblesse mass spectrometer. The measurements were carried out at 250 μA 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.

Large ^{20}Ne beams (>100,000 cps) were measured on a Faraday cup. An automated liquid nitrogen trap was used to keep the Ar and CO_2 backgrounds low and we corrected for isobaric interferences from doubly-charged Ar and CO_2. The $^{40}Ar^{++}/^{40}Ar^{+}$ and CO_2^{++}/CO_2^{+} ratios were 0.031±0.003 and 0.0045±0.0005, respectively, and the $^{40}Ar^{++}$ and 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}Ar and the axial and low mass multipliers for ^{38}Ar and ^{36}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}He, ^{22}Ne, ^{36}Ar and ^{130}Xe were all below 1.5×10^{-11}, 1.06×10^{-13}, 8.1×10^{-13}, and 1.3×10^{-16} cm^3 STP, respectively, but typically were 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 $^{4}He/^{3}He$ ratio of 81,700 (8.81 R_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 1σ uncertainty.

3. Results

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

147

148 *3.1. Measured Ne, Ar and Xe isotopic ratios*

149 We measured $^{20}Ne/^{22}Ne$ ratios of up to 12.22 ± 0.03 (1σ) and $^{21}Ne/^{22}Ne$ ratios up to
150 0.0430 ± 0.0002 (1σ) in the NLD 27 sample with a $^{4}He/^{3}He$ ratio of 46,700 (15.4 R_A). Measured
151 $^{40}Ar/^{36}Ar$ ratios vary up to 9269 ± 93 (1σ) in the same sample, which is close to measured
152 $^{40}Ar/^{36}Ar$ ratios of up to 11,988 ± 156 at the PPT seamount off Samoa (Poreda and Farley, 1992).
153 The maximum measured $^{40}Ar/^{36}Ar$ value in NLD 13, which has a $^{4}He/^{3}He$ ratio of 25,600 (28.1
154 R_A) is 4828 ± 48. We find measured $^{129}Xe/^{130}Xe$ excesses with respect to the atmospheric
155 composition in all 4 of the Rochambeau samples. The highest measured $^{129}Xe/^{130}Xe$ is 6.93 ±
156 0.03 (1σ) from NLD 13 and represents the largest excess yet recorded in a basalt with a $^{4}He/^{3}He$
157 ratio as low as 25,600 (Supplemental Table 2).

158

159 *3.2. Ne, Ar and Xe isotopic composition of the Rochambeau Rift mantle source*

160 Shallow-level air contamination affects all Ne, Ar, and Xe isotopic measurements in
161 mantle-derived basalts (e.g., Sarda et al., 1985; Honda et al., 1993; Farley and Neroda, 1998).
162 Accurately interpreting differences in noble gas compositions of mantle sources requires
163 correcting for the shallow level atmospheric contaminant. We correct for the atmospheric
164 contaminant through least-squares fitting of well-defined arrays in $^{21}Ne/^{22}Ne$-$^{20}Ne/^{22}Ne$,
165 $^{20}Ne/^{22}Ne$-$^{40}Ar/^{36}Ar$ and $^{40}Ar/^{36}Ar$-$^{129}Xe/^{130}Xe$ space. The fits are then extrapolated to the mantle
166 $^{20}Ne/^{22}Ne$ ratio. Correction for air contamination is a least-squares linear extrapolation for
167 $^{21}Ne/^{22}Ne$ (Figs. 2 and 3). For mantle $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ the corrections are least-squares
168 hyperbolic extrapolations (Figs. 4 and 5).

169 While recent work based on continental well gas and the gas-rich popping rock from the
170 north mid-Atlantic Ridge suggests that the MORB source has a $^{20}Ne/^{22}Ne$ of 12.5 (Ballentine et
171 al., 2005; Holland and Ballentine, 2006; Raquin et al., 2008), the Iceland (Mukhopadhyay, 2012)
172 and Kola plume (Yokochi and Marty, 2004) have a solar $^{20}Ne/^{22}Ne$ ratio. Therefore, the mantle
173 $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ of the Rochambeau Rift samples were determined by projecting the best
174 fit line through the step crushes to the OIB-MORB mixing line (Fig. 2). We denote the
175 extrapolated mantle source $^{21}Ne/^{22}Ne$ ratio as $^{21}Ne/^{22}Ne_E$. The mantle source $^{20}Ne/^{22}Ne$
176 determined from the intersection of the OIB-MORB mixing line with the best fit line through the
177 sample data is used to extrapolate the hyperbolic fits in Ar and Xe isotopic space to the
178 corresponding mantle source value (Figs. 4 and 5). We note that extrapolating Ar and Xe
179 isotopic ratios to a mantle $^{20}Ne/^{22}Ne$ of 12.5 does not affect our overall conclusions.

180 The *x* and *y* error weighted linear least square fits (Mukhopadhyay, 2012; Tucker et al., in
181 press) through the Ne data yield mantle $^{21}Ne/^{22}Ne_E$ values ranging between 0.042 and 0.048 (Fig.
182 2). Thus, all of the Rochambeau samples are less nucleogenic than the N. Mid-Atlantic Ridge
183 popping rock ($^{21}Ne/^{22}Ne_E$ = 0.06; Moreira et al., 1998) and the depleted MORBs from the
184 Equatorial Atlantic (0.062-0.065; Tucker et al., in press).

185 To determine the mantle source Ar and Xe isotopic ratios corrected for shallow-level
186 atmospheric contamination, we only use sample NLD 27, for which a relatively large number of
187 steps yield a well-defined hyperbola (Figs. 4 and 5; Supplemental Tables 1 and 2). The
188 extrapolated mantle $^{40}Ar/^{36}Ar$ ratio ($^{40}Ar/^{36}Ar_E$) is 16,763 ± 1,144. The $^{40}Ar/^{36}Ar$ ratio of the
189 Rochambeau source is significantly lower than the estimated source values of 27,000 ± 4000 for
190 popping rock (Raquin et al., 2008), 41,050 ± 2670 for the Bravo Dome well gas (Holland and
191 Ballentine, 2006) and 41,500 ± 9000 for the depleted equatorial Atlantic MORBs (Tucker et al.,

192 In press). The $^{40}Ar/^{36}Ar_E$ for the Rochambeau sample is higher than the Iceland plume source
193 $^{40}Ar/^{36}Ar_E$ of 10,732 ± 3080 (Mukhopadhyay, 2012). While we do not have sufficient number of
194 step crushes for NLD 13 and NLD 14 to independently constrain the mantle source value for
195 these two samples, the step crush data do in general fall on the hyperbolic best fit line for NLD
196 27 (Fig 4). Hence, all of the samples may have similar mantle source $^{40}Ar/^{36}Ar$ values.

197 The hyperbolic fit for NLD 27 in Ar-Xe space yields a mantle source value of 6.92 ±
198 0.07, similar to the maximum measured values at the Rochambeau Rift and in the Samoan
199 xenoliths (Fig. 5). The mantle source value for NLD 27 is significantly lower than source values
200 of 7.6 for popping rock (Moreira et al., 1998), 7.9 ± 0.14 for Bravo Dome (Holland and
201 Ballentine, 2006) and 7.77 ± 0.06 for depleted equatorial Atlantic MORBs (Tucker et al., In
202 press). The composition of NLD 27, however, overlaps with the Iceland composition of 6.98 ±
203 0.07 (Mukhopadhyay, 2012). NLD 13 appears to have higher $^{129}Xe/^{130}Xe$ ratios for a given
204 $^{40}Ar/^{36}Ar$ ratio and thus, may have a higher mantle source value than NLD 27 although
205 additional data will be required to verify this claim. In any case, our observations confirm that
206 the measured $^{129}Xe/^{130}Xe$ ratios are not a result of shallow-level (post-eruptive) air contamination
207 but are a characteristic of the plume source.

208

209 **4. Relationships between elemental ratios and isotopic ratios**

210 *4.1. Helium-Neon in the Rochambeau Rift source*

211 The $^{4}He/^{3}He$ and $^{21}Ne/^{22}Ne_E$ isotopic compositions of the four Rochambeau samples
212 show the influence of a mantle plume, and the He-Ne isotopic ratios can be explained by mixing
213 between a less degassed mantle source (e.g., FOZO) and a depleted MORB source (Figs. 2 and

3). As seen in Figure 3, for a given $^{4}He/^{3}He$ ratio, the Rochambeau samples have a higher $^{21}Ne/^{22}Ne_{E}$ 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., 1993; Valbracht et al., 1996; Jackson et al., 2009; Poreda and Farley, 1992). The higher $^{21}Ne/^{22}Ne$ at a given $^{4}He/^{3}He$ ratio reflects a higher time-integrated $^{3}He/^{22}Ne$ in the mantle source of the Rochambeau basalts compared to plume sources at Iceland and Galapagos. A high $^{3}He/^{22}Ne$ in the Lau back-arc source has been previously noted (Hahm et al., 2012; Honda et al., 1993; Lupton et al., 2012), and there are at least two possible explanations for the high $^{3}He/^{22}Ne$ in the Rochambeau Rift samples compared to Iceland and Galapagos:

i) The plume material that flows into the Rochambeau Rift has a higher $^{3}He/^{22}Ne$ ratio than the Iceland and Galapagos plumes and mixes with the depleted back-arc mantle. Such an explanation, however, requires that $^{3}He/^{22}Ne$ differences exist between plumes. Since mantle $^{3}He/^{22}Ne$ ratios are difficult to perturb, such variations may point to preservation of heterogeneities from the first few hundred million years of Earth's history within the deep mantle (Honda et al., 1993; Kurz et al. 2009; Mukhopadhyay 2012; Yokochi and Marty 2005).

ii) The apparently high $^{3}He/^{22}Ne$ ratio results from mixing between a plume source with low $^{3}He/^{22}Ne$ (~3) and a back-arc mantle with $^{3}He/^{22}Ne$ that is elevated with respect to the MORB source. We note that high $^{3}He/^{22}Ne$ ratios have also been observed in the Manus back-arc basin (Shaw et al., 2001). The reason why these back-arc basins may have high $^{3}He/^{22}Ne$, however, is uncertain.

4.2. Two mantle sources inferred from Helium-Argon relationships

The most gas rich sample in our study, NLD 27, has a $^{4}He/^{40}Ar^{*}$ ratio of 3.3 (where '*' indicates radiogenic), which is within the range of 1.6-4.2 expected for the mantle production ratio. Hence, NLD 27 preserves relatively unfractionated mantle noble gas elemental ratios and we focus on this sample for the rest of the manuscript. The step crushes from NLD 27 demonstrate excellent correlation between $^{3}He/^{36}Ar$ and $^{40}Ar/^{36}Ar$ ratios (Fig. 6a), where ^{3}He and ^{36}Ar are primordial. The $^{3}He/^{36}Ar$ ratio of 1.33 for the NLD 27 source is higher than both the popping rock and Bravo Dome well gas sources, which have $^{3}He/^{36}Ar$ ratios of 0.4 and 0.3, respectively (Holland and Ballentine, 2006; Moreira et al., 1998). The $^{3}He/^{36}Ar$ ratio of the mantle can decrease over time because of preferential recycling of atmospheric Ar (Fig 6a). Thus, the higher $^{3}He/^{36}Ar$ in Iceland and Rochambeau plumes relative to MORBs cannot be related to recycling of atmospheric noble gases into a MORB-like mantle source. Likewise, since mixing in the $^{3}He/^{36}Ar$-$^{40}Ar/^{36}Ar$ space is linear, adding recycled atmospheric Ar to MORBs does not explain the low $^{40}Ar/^{36}Ar$ ratios of the plume sources (Fig. 6a). Consequently, a less degassed source is required to explain the lower $^{40}Ar/^{36}Ar$ ratio of the plume source.

The Iceland, Galapagos, and Rochambeau samples define very similar slopes in $^{3}He/^{36}Ar$-$^{40}Ar/^{36}Ar$ space even though the Rochambeau source has a higher $^{3}He/^{22}Ne$. While the Ne-Ar measurements from Galapagos do not yet constrain the mantle $^{40}Ar/^{36}Ar$ ratio in the Galapagos plume (Raquin and Moreira, 2009), the Iceland source has lower $^{40}Ar/^{36}Ar$ and $^{3}He/^{36}Ar$ ratios than the Rochambeau source. If the measured values at Galapagos are reflective of a low $^{40}Ar/^{36}Ar$ ratio in the mantle source, then both the Galapagos and Iceland source compositions could be related to the Rochambeau plume 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 reservoir in the plume source.

260

261 *4.3. Ancient MORB-OIB separation inferred from Helium-Xenon relationships*

262 Similar to the $^{3}He/^{36}Ar$ and $^{40}Ar/^{36}Ar$ correlation, the $^{129}Xe/^{130}Xe$ ratios from the
263 individual step crushes on NLD 27 show an excellent correlation with the $^{3}He/^{130}Xe$ ratios (Fig.
264 6b). We note that ^{3}He and ^{130}Xe are primordial, while ^{129}Xe is produced from decay of extinct
265 ^{129}I. The $^{129}Xe/^{130}Xe$ ratio, therefore, stopped evolving 100 Myr after the start of the Solar
266 System.

267 The data in Figure 6b demonstrate that, compared to the MORB source, the Rochambeau
268 and Iceland mantle sources evolved with different I/Xe ratios. The step crushes from the NLD 27
269 sample displays a slope that is quite distinct from the gas-rich MORB 2ΠD43 (popping rock),
270 but is similar to the correlation defined by Iceland. Since mixing in $^{3}He/^{130}Xe$-$^{129}Xe/^{130}Xe$ space
271 is linear, adding subducted atmospheric Xe to the MORB-source will move the source
272 composition towards air along a straight line (Fig. 6b). Hence, adding subducted atmospheric Xe
273 to the MORB source clearly cannot produce the Rochambeau and Iceland mantle source
274 compositions (Fig. 6b). Similarly, the Rochambeau and Iceland source cannot supply Xe to the
275 MORB source unless radiogenic ^{129}Xe is added to the plume Xe isotopic composition. However,
276 ^{129}I became extinct at ~4.45 Ga. As a result, the difference in MORB and plume $^{129}Xe/^{130}Xe$
277 ratios must have been set up early and the last major equilibration between the two reservoirs
278 must have predated 4.45 Ga as otherwise the differences in $^{129}Xe/^{130}Xe$ would not have been
279 preserved in the present-day mantle. We conclude that plumes *cannot* supply Xe and all of the
280 primordial volatiles to the MORB source.

281

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}Xe that was produced from decay of extinct ^{129}I, ^{136}Xe was produced by spontaneous fission of now extinct ^{244}Pu (half-life = 80 Myr). However, ^{136}Xe is also generated by spontaneous fission of extant ^{238}U. Thus, the I-Xe and Pu-Xe systems are sensitive to the first ~100 Ma and 500 Ma of Earth history, respectively, while the U-Xe system evolves throughout Earth history.

The error-weighted mean xenon isotope composition (^{129}Xe/^{136}Xe vs. ^{130}Xe/^{136}Xe) of NLD 27, of all four of the Rochambeau samples, Iceland (Mukhopadhyay, 2012), MORBs from the Southwest Indian Ridge (Parai et al., In revision) and MORBs from the Equatorial Atlantic (Tucker et al., In press) are shown in Figure 7. Our observations demonstrate that MORBs and plumes have small but distinct differences in ^{129}Xe/^{136}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 Figure 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., In press), we emphasize that recycling by itself cannot explain the ^{129}Xe/^{136}Xe isotopic difference between MORBs and plumes. Likewise,

304 mixing MORB Xe with fissiogenic ^{136}Xe in recycled slabs will lead to a decrease in the
305 ^{129}Xe/^{136}Xe ratio. Hence, plume Xe cannot be a mixture of MORB and fissiogenic Xe.

306 The ^{129}Xe/^{136}Xe ratio is a measure of the time integrated ^{129}I/(^{244}Pu+^{238}U) ratio and the
307 differences in the Xe isotopic composition between the different basalt groups (Fig. 7) can be
308 explained by mantle processing and mixing of less degassed and more degassed mantle sources.
309 A mantle reservoir that undergoes degassing after I and Pu are extinct will have low
310 concentrations of primordial ^{130}Xe, radiogenic ^{129}Xe and fissiogenic ^{136}Xe produced by extinct
311 ^{244}Pu. Addition of ^{136}Xe from ^{238}U fission to such a degassed source would decrease both the
312 ^{129}Xe/^{136}Xe and the ^{130}Xe/^{136}Xe ratios of the reservoir (Fig. 7b). Hence, we conclude that the
313 MORB sources are more degassed than the plume sources, a conclusion that is based only on the
314 Xe isotopic ratios and independent of the absolute concentration of noble gases or the
315 partitioning of noble gases with respect to their radiogenic parents.

316

317 *5.1. Pu-U-I systematics in the Rochambeau Rift source*

318 The ^{244}Pu- and ^{238}U-produced fission isotopes of Xe (^{131,132,134,136}Xe) provide information
319 about mantle processing rates, particularly during the Hadean (e.g., Allegre et al., 1987; Coltice
320 et al., 2009; Kunz et al., 1998; Ozima et al., 1985; Yokochi and Marty, 2005). ^{244}Pu and ^{238}U
321 produce the four fission isotopes in different proportions and fission Xe yields from Pu are
322 significantly larger than from U. A reservoir that has remained completely closed to volatile loss
323 over Earth's history will have $^{136}Xe_{Pu}$*/$^{136}Xe_{U}$* of ~27, where '*' refers to fissiogenic Xe
324 (Tolstikhin et al., 2006; Tolstikhin and O'Nions, 1996). ^{244}Pu became extinct at ~4 Ga and
325 reservoirs that underwent extensive degassing over the past 4 Ga would have lost a significant
326 fraction of the Pu-produced fission Xe and, thus, have a large proportion of ^{238}U-derived fission

Xe; i.e., $^{136}Xe_{Pu}$*/$^{136}Xe_{U}$* in degassed reservoirs will be << 27. Consequently, deconvolving ^{244}Pu- from ^{238}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}U- from ^{244}Pu-derived fissiogenic Xe, five Xe isotopes were used (^{130,131,132,134,136}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 composition for the fission isotopes, the ^{129}Xe/^{132}Xe ratios in the individual steps were regressed against the ^{40}Ar/^{36}Ar ratio using a least squares hyperbolic fit, which yielded a mantle ^{129}Xe/^{132}Xe ratio of 1.038 at a ^{40}Ar/^{36}Ar of 16,763 (Supplemental Figure 1). Next, the ^{130,131,134,136}Xe/^{132}Xe ratios in the individual crushing steps were regressed against the ^{129}Xe/^{132}Xe ratio. From the slopes and uncertainties in the slopes, the mantle ^{130,131,134,136}Xe/^{132}Xe ratios, along with their uncertainties, were calculated for a mantle ^{129}Xe/^{132}Xe ratio of 1.038 for the Rochambeau source (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}Xe/^{136}Xe distinct from the atmospheric composition at the 2σ 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 $Ax = b$ was found with the following additional constraints: $\Sigma x_i = 1$ and $0 \leq x_i \leq 1$ (also see Caffee et al., 1999; Mukhopadhyay, 2012). Here, A defines the composition of the end-members, x the fraction of each component, and b the sample composition. 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 1σ 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) $^{128}Xe/^{130}Xe$ 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 are listed in Supplemental Table 3.

Depending on whether the initial mantle Xe is solar or chondritic, the fraction of ^{136}Xe derived from ^{244}Pu fission is 0.87±0.11 or 0.85±0.14, respectively (Table 1). The Pu-derived ^{136}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, 2012). The values for the Kola plume were inferred based on elemental correlations between ^{4}He-^{21}Ne-^{136}Xe, and the lower values at Kola may arise in part because elemental ratios can be fractionated through a combination of solubility and diffusivity controlled degassing (Gonnermann and Mukhopadhyay, 2007; Paonita and Martelli, 2007; Yokochi and Mary, 2005). The Iceland and Rochambeau plume values are higher than values of 0.25 to 0.29 for the depleted MORB source (Tucker et al., in press; 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}Pu-derived ^{136}Xe in plumes is a robust result. A higher fraction ^{244}Pu-derived ^{136}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 $^{129}Xe^*/^{136}Xe_{Pu}^*$ ratio, where $^{129}Xe^*$ is the decay product of ^{129}I decay and $^{136}Xe_{Pu}^*$ is ^{136}Xe produced from ^{244}Pu fission (Allegre 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 Allegre, 1982; Yokochi and Marty, 2005). Since ^{129}I has a shorter half-life than ^{244}Pu, higher $^{129}Xe^*/^{136}Xe_{Pu}^*$ ratios are indicative of earlier closure to volatile loss. We find that for the Rochambeau source, the $^{129}Xe^*/^{136}Xe_{Pu}^*$ ratio is $2.9^{+0.6}_{0.4}$ to $3.2^{+1.2}_{0.4}$ (Table 2). While detailed modeling of the fission and radiogenic Xe isotopes is beyond the scope of this paper, we note that the $^{129}Xe^*/^{136}Xe_{Pu}^*$ 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 homogenous I/Pu ratio, the higher $^{129}Xe^*/^{136}Xe_{Pu}^*$ 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 $^{129}Xe^*/^{136}Xe_{Pu}^*$ in the Rochambeau and Iceland source 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 observation from Iceland and Rochambeau is that plumes have lower $^{129}Xe/^{130}Xe$ ratio than MORBs and that the difference cannot be related solely through recycling of atmospheric noble gases. This observation requires that the reservoirs supplying noble gases to plumes and MORBs were processed and outgassed to different extents within the first 100 million years 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 the $^{129}Xe/^{130}Xe$ ratio.

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 over Earth's history with primitive He isotopic signatures (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}He, ^{22}Ne, ^{36}Ar and ^{130}Xe and radiogenic ^{129}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 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, elemental abundance ratios are expected to be the same in the two sources. However, the Iceland plume has different elemental abundances than MORBs (Mukhopadhyay, 2012). Our Rochambeau data also show differences from MORBs. For example, the $^{3}He/^{36}Ar$ 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, $^{129}Xe/^{130}Xe$ ratio in the plume source is higher than in the MORB source, a prediction that is clearly refuted by our observations of lower $^{129}Xe/^{130}Xe$ in the plume source. As noted earlier, the lower $^{129}Xe/^{130}Xe$ ratio in the plume source cannot arise solely from recycling. Thus, we suggest that all of the primordial gases and the radiogenic ^{129}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-looking' reservoir

In contrast to many models that assign the low $^{4}He/^{3}He$ ratios observed in many OIBs to a primordial reservoir, Lee et al. (2010) suggested that a 'primordial-looking' reservoir could have been produced during the first billion years of Earth's history through a process termed upside-down differentiation. Lee et al. (2010) suggest that a hotter mantle during the Hadean and earliest Archean leads to partial melting at depths between 660 and 410 km, producing Fe-rich melts. At these depths, 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 U/^{3}He, ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, ^{206}Pb/^{204}Pb today, i.e., a 'primordial-looking' reservoir (Lee et a., 2010). As the noble gases are incompatible (e.g., Heber et al., 2007), the model predicts that the primordial noble gas elemental ratios (e.g., ^{3}He/^{22}Ne, ^{3}He/^{36}Ar) of the melts would be the same as the solid convecting mantle. Importantly, differences in ^{129}Xe/^{130}Xe between the MORB source and the low ^{4}He/^{3}He reservoir are not expected, since the process of generating the 'primordial' reservoir occurs over for 1 Gyr, well past the 100 Ma lifetime of ^{129}I.

MORBs and low ^{4}He/^{3}He plumes, however, have different elemental ratios (Fig. 6; also see Mukhopadhyay, 2012). Furthermore, the ^{20}Ne/^{22}Ne ratio of the plume and MORB sources is different (Mukhopadhyay, 2012; Yokochi and Marty, 2004). Since Ne is not subducted back to the mantle in significant quantities, the difference in ^{20}Ne/^{22}Ne is related to Earth's accretion (Ballentine et al., 2005; Mukhopadhyay, 2012) and cannot result from melting processes. Furthermore, the ^{129}Xe/^{130}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}Xe/^{130}Xe ratio, or have ^{129}Xe/^{130}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 noble gas signature seen in mantle plumes.

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-looking 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 are heavier than the peridotites and are assumed to sink to the D" region and are sequestered there for long periods of time. Because the geochemical consequences for the noble gases are the same as the upside-down differentiation model (Lee et al. 2010), the same arguments presented above allow us to rule out Davies' (2010) hypothesis as the primary mechanism for generating the primitive-looking OIB reservoir.

Several studies have suggested that the primitive-looking $^{4}He/^{3}He$ ratios in OIBs are signatures of depleted residues of mantle melting because U is more incompatible than He (e.g., Coltice and Ricard, 1999; Parman et al., 2005). In such scenarios, separation of the MORB and low $^{4}He/^{3}He$ reservoirs is not required over Earth's history. Rather, because the residues have very low $U/^{3}He$ ratios, the $^{4}He/^{3}He$ ratio of the convecting mantle gets frozen in the residues. For residues generated at 2-3 Ga, the convecting mantle $^{4}He/^{3}He$ could have the same values as observed in many OIBs. Our results from Iceland and Rochambeau suggest that if low $^{4}He/^{3}He$ ratios in OIBs are indeed due to sampling of depleted residues of mantle melting, then the $^{129}Xe/^{130}Xe$ ratios require the depleted residues to be generated prior to 4.45 Ga. In other words, the low $^{4}He/^{3}He$ reservoir has essentially behaved as a closed system over Earth's history.

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

Several recent studies have suggested that plumes might originate from the LLSVPs at the base of the mantle (e.g., Burke, 2011; Dziewonski et al., 2010; Torsvik et al., 2010). Both primitive (Deschamps et al., 2011; Jackson and Carlson, 2011; Mukhopadhyay 2012) 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.

Our observation that the Rochambeau and Iceland plume sources have high proportions of Pu-derived fission Xe as well as recycled atmospheric Xe requires that plumes sample both primitive and recycled material. We note that the DICE 10 sample from Iceland has amongst the most primitive $^{21}Ne/^{22}Ne$ 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 $^{4}He/^{3}He$ ratio plume basalts as a direct measure of the composition of primitive mantle (Jackson et al., 2010; Jackson and Carlson, 2011).

7. Conclusions

We measured He, Ne, Ar, and Xe abundances and isotopic compositions of four plume influenced basalts with low $^{4}He/^{3}He$ ratios from the Rochambeau Rift in the northern Lau back-arc basin. We documented that sample NLD 13 with a $^{4}He/^{3}He$ ratio of 25,600 (28.1 R_A) has a

509 $^{40}Ar/^{36}Ar$ ratio of at least 4828 and $^{129}Xe/^{130}Xe$ ratio of at least 6.93 ± 0.03. For NLD 27, which
510 had a sufficient number of step crushes, we infer mantle source $^{40}Ar/^{36}Ar$ ratio of 16,763 ± 1,144
511 and $^{129}Xe/^{130}Xe$ ratio of 6.92±0.07. These values are consistent with the mantle plume at the
512 Rochambeau Rift to be from Samoa (also see Poreda and Farley, 1992).

513 The new results from the Lau basin confirm the Xe isotopic findings from Iceland that
514 the plume reservoir has a low $^{129}Xe/^{130}Xe$ that cannot result solely from adding subducted
515 atmospheric Xe to MORB Xe. Rather, the plume source has a lower I/Pu ratio compared to the
516 MORB source. Given the short half-life of ^{129}I, the result suggests that the plume source was
517 more volatile-poor compared to the MORB source and the two reservoirs were separated from
518 each other within the first 100 million years of Earth's history. Subsequent to this period, the two
519 reservoirs could not have been homogenized as otherwise the difference in $^{129}Xe/^{130}Xe$ would
520 not be preserved in the present-day mantle. Models that seek to explain the dynamical and
521 chemical evolution of the mantle must be compatible with these results. For example, if plumes
522 are indeed derived from LLSVPs, then the Xe data require LLSVPs to have existed since 4.45
523 Ga.

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527 **References**

528 Allegre C., Hofmann A., ONions K., 1996. The Argon constraints on mantle structure. Geophys.
529 Res. Lett. 23, 3555–3557.
530 Allegre C., Staudacher T., Sarda P., 1987. Rare Gas Systematics: Formation of the Atmosphere,
531 Evolution and Structure of the Earth's Mantle. Earth Planet. Sci. Lett. 81, 127–150.
532 Azbel, I. Y., Tolstikhin, I., 1993. Accretion and early degassing of the Earth: Constraints from

Pu-UI-Xe isotopic systematics. Meteoritics 28, 609–621.

Ballentine, C. J., Holland, G., 2008. What CO_2 well gases tell us about the origin of noble gases in the mantle and their relationship to the atmosphere. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 366, 4183–4203.

Ballentine C. J., et al., 2005. Neon isotopes constrain convection and volatile origin in the Earth's mantle. Nature 433, 33-38.

Caffee M. W., et al., 1999. Primordial Noble Gases from Earth's Mantle: Identification of a Primitive Volatile Component. Science 285, 2115–2118.

Coltice N., Ricard Y., 1999. Geochemical observations and one layer mantle convection. Earth Planet. Sci. Lett. 174, 125-137.

Coltice N., Marty B., Yokochi R., 2009. Xenon isotope constraints on the thermal evolution of the early Earth. Chem. Geol., 266, 4-9.

Davies, G. F., 2010. Noble gases in the dynamic mantle. Geochemistry Geophysics Geosystems 11, Q03005, DOI: 3010.01029/02009GC002801.

Deschamps F., Kaminski E., Tackley P. J., 2011. A deep mantle origin for the primitive signature of ocean island basalt, Nature Geoscience 4, 879-882.

Dixon E. T., Honda M., McDougall I.H., 2000. Preservation of near-solar neon isotopic ratios in Icelandic basalts. Earth Planet. Sci. Lett. 180, 309–324.

Farley K. A. and Neroda E., 1998. Noble gases in the Earth's mantle. Ann. Rev. Earth Planet. Sci. 26, 189-218.

Farley K. A., Natland J. H., Craig H., 1992. Binary mixing of enriched and undegassed (primitive?) mante components (He, Sr, Nd, Pb) in Samoan lavas. Earth Planet. Sci. Lett. 111, 183-199.

Gayer E., Mukhopadhyay S., Meade B. J., 2008. Spatial variability of erosion rates inferred from the frequency distribution of cosmogenic ^{3}He in olivines from Hawaiian river sediments. Earth Planet. Sci. Lett. 266, 303-315.

Gonnermann H. M., Mukhopadhyay S., 2009. Preserving noble gases in a convecting mantle. Nature 459, 560–563.

Gonnermann H. M., Mukhopadhyay, S., 2007. Non-equilibrium degassing and a primordial source for helium in ocean–island volcanism. Nature 449, 1037–1040.

Graham D. W., et al., 2001. Upper mantle dynamics revealed by helium isotope variations along

564 the Southeast Indian Ridge. Nature 409, 701-703.
565 Graham D. W., 2002. Noble gas isotope geochemistry of mid-ocean ridge and ocean island
566 basalts: characterization of mantle source reservoirs. In Porcelli D., Ballentine C. J.,
567 Wieler R. (Eds). Noble gases in geochemistry and cosmochemistry: Reviews in
568 Mineralogy and Geochemistry, vol 47, 247-318.
569 Hahm D., et al., 2012. An overview of the volatile systematics of the Lau basin- Resolving the
570 effects of source variation, magmatic degassing and crustal contamination. Geochim.
571 Cosmochim. Acta 85, 88-113.
572 Hanyu T., et al., 2001. Noble gas study of the Reunion hotspot: evidence for distinct less-
573 degassed mantle sources. Earth Planet. Sci. Lett, 193, 83-98.
574 Heber V. S., et al., 2007. Crystal-melt partitioning of noble gases (helium, neon, argon, krypton,
575 and xenon) for olivine and clinopyroxene. Geochim. Cosmochim. Acta 71, 1041-1061.
576 Hilton D. L., et al., 1993. Helium and argon isotope systematics from the central Lau Basin and
577 Valu Fa Ridge: evidence of crust/mantle interactions in a back-arc basin. Geochim.
578 Cosmochim. Acta 57, 2819-2841.
579 Holland G., Ballentine C. J., 2006. Seawater subduction controls the heavy noble gas
580 composition of the mantle. Nature 441, 186–191.
581 Holland G., Cassidy M., Ballentine C. J., 2009. Meteorite Kr in Earth's Mantle Suggests a Late
582 Accretionary Source for the Atmosphere. Science 326, 1522–1525.
583 Honda M., et al., 1993. Noble gases in submarine pillow basalt glasses from the Lau Basin:
584 detection of a solar component in backarc basin basalts. Earth Planet. Sci. Lett. 120, 135–
585 148.
586 Honda M., et al., 1993. Noble gases in submarine pillow basalts from Loihi and Kilauea, Hawaii:
587 A solar component in the Earth. Geochim. Cosmochim. Acta 57, 858-874.
588 Hutko A., et al., 2006, Seismic detection of folded, subducted lithosphere at the core-mantle
589 boundary. Nature 441, 333–336.
590 Jackson M. G., Kurz M. D., Hart S. R., Helium and neon isotopes in phenocrysts from Samoan
591 lavas: Evidence for heterogeneity in the terrestrial high $^{3}He/^{4}He$ mantle. Earth Planet. Sci.
592 Lett. 287, 519-528.
593 Jackson M. G., et al., 2007. New Samoan lavas from Ofu Island reveal a hemispherical
594 heterogeneous high $^{3}He/^{4}He$ mantle. Earth Planet. Sci. Lett. 264, 360-374.

595 Kellogg L. H., Wasserburg G. J., 1990. The role of plumes in helium fluxes. Earth Planet. Sci.
596 Lett. 99, 276-289.
597 Kendrick M.A., et al., 2011. High abundances of noble gas and chlorine delivered to the mantle
598 by serpentinite subduction. Nature Geoscience 4, 807–812.
599 Kunz J., Staudacher T., Allègre C.J., 1998. Plutonium-fission xenon found in Earth's mantle.
600 Science 280, 877–880.
601 Kurz M. D., Jenkins W., Hart S., 1982. Helium Isotopic Systematics of Oceanic Islands and
602 Mantle Heterogeneity. Nature 297, 43–47.
603 Kurz M. D., et al., 2009. Primitive neon from the center of the Galapagos hotspot. Earth Planet.
604 Sci. Lett. 286, 23-34.
605 Lee C. T. A., et al., 2010. Upside-down differentiation and generation of a 'primordial' lower
606 mantle. Nature 463, 930-933.
607 Leya I., Wieler R., 1999. Nucleogenic production of Ne isotopes in Earth's crust and upper
608 mantle induced by alpha particles from the decay of U and Th. J. Geophys. Res. 104,
609 15439-15450.
610 Lupton J. E., et al., 2012. Mantle hotspot neon in basalts from the Northwest Lau back-arc basin.
611 Geophys. Res. Lett. 39, L08308, doi:10.1029/2012GL051201.
612 Lupton J. E. et al., 2009. Helium isotope variations in seafloor basalts fromm the northwest Lau
613 back-arc basin: Mapping the influence of the Samoan plume. Geophys. Res. Lett. 36,
614 L1731, doi:10.1029/2009GL039468.
615 Mahoney J. J., et al., 1993. Isotope and trace element characteristics of a super-fast spreading
616 ridge: East Pacific Rise, 13-238S. Earth Planet. Sci. Lett. 121, 173- 193.
617 Marty B., 1989. Neon and Xenon Isotopes in MORB: implications for the earth-atmosphere
618 evolution. Earth Planet. Sci. Lett. 94, 45–56.
619 Millen D. W., Hamburger M. W., 1998. Seismological evidence for tearing of the Pacific plate at
620 the northern termination of the Tonga subduction zone. Geology 26, 659-662.
621 Moreira M., Kunz J., Allegre C., 1998. Rare gas systematics in popping rock: Isotopic and
622 elemental compositions in the upper mantle. Science 279, 1178–1181.
623 Moreira M., et al., 2001. Solar neon in the Icelandic mantle: new evidence for an undegassed
624 lower mantle. Earth Planet. Sci. Lett. 185, 15–23.
625 Mukhopadhyay, S., 2012. Early differentiation and volatile accretion recorded in deep-mantle

neon and xenon. Nature 486, 101–104.

Ozima M., Podosek F., Igarashi G., 1985. Terrestrial xenon isotope constraints on the early history of the Earth. Nature 315, 471–474.

Parman S.W., 2007. Helium isotopic evidence for episodic mantle melting and crustal growth. Nature 446, 900-903.

Paonita A., Martelli M., 2007. A new view of the He-Ar-CO_2 degassing at mid-ocean ridges: Homogeneous composition of magmas from the upper mantle. Geochim. Cosmochim Acta 71, 1747-1763.

Pepin R.O., 1991. On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. Icarus 92, 2–79.

Pepin R. O., Porcelli D., 2006. Xenon isotope systematics, giant impacts, and mantle degassing on the early Earth. Earth Planet. Sci. Lett. 250, 470–485.

Porcelli D., Wasserburg G., 1995. Mass transfer of helium, neon, argon, and xenon through a steady-state upper mantle. Geochim. Cosmochim. Acta 59, 4921–4937.

Poreda R. J., Farley K. A., 1992. Rare gases in Samoan xenoliths. Earth Planet. Sci. Lett. 113, 129-144.

Poreda R. J., Craig H., 1991. He and Sr isotopes in the Lau basin mantle – Depleted and primitive mantle components. Earth Planet. Sci. Lett. 113, 487-493.

Pujol M., Marty B., Burgess R., 2011. Chondritic-like xenon trapped in Archean rocks: A possible signature of the ancient atmosphere. Earth Planet. Sci. Lett. 308, 298–306.

Raquin A., Moreira M., 2009. Atmospheric $^{38}Ar/^{36}Ar$ in the mantle: Implications for the nature of the terrestrial parent bodies. Earth Planet. Sci. Lett. 287, 551–558.

Raquin A., Moreira M., Guillon F., 2008. He, Ne and Ar systematics in single vesicles: Mantle isotopic ratios and origin of the air component in basaltic glasses. Earth Planet. Sci. Lett. 274, 142–150.

Regelous M., et al., 2008. Mantle dynamics and mantle melting beneath Niuafo'ou Island and the northern Lau back-arc basin, Contrib. Mineral. Petrol. 156, 103–118.

Sarda P., Staudacher T., Allegre C. J., 1985. $^{40}Ar/^{36}Ar$ in MORB glasses - constraints on atmosphere and mantle evolution. Earth Planet. Sci. Lett. 72, 357-375.

Shaw A. M., et al., 2001. Nucleogenic neon in high $^{3}He/^{4}He$ lavas from the Manus back-arc basin: a new perspective on He-Ne decoupling. Earth Planet. Sci. Lett 194, 53-66.

657 Smith G. P., et al., 2001. A complex pattern of mantle flow in the Lau backarc. Science 292,
658 713-716.
659 Staudacher T., Allegre C. J., 1982. Terrestrial xenology. Earth Planet. Sci. Lett. 60, 389-406.
660 Stuart F. M., et al., 2003. High $^{3}He/^{4}He$ ratios in picritic basalts from Baffin Island and the role
661 of a mixed reservoir in mantle plumes. Nature 424, 57-59.
662 Sumino H., et al., 2010. Seawater-derived noble gases and halogens preserved in exhumed
663 mantle wedge peridotite. Earth Planet. Sci. Lett. 294, 163–172.
664 Tackley P. J., 2011. Living dead slabs in 3-D: The dynamics of compositionally-stratified slabs
665 entering a "slab graveyard" above the core-mantle boundary. Phys. Earth Planet. Interiors
666 188, 150-162.
667 Tan E., Gurnis M., 2005. Metastable superplumes and mantle compressibility. Geophys. Res.
668 Lett. L20307, doi: 10.1029/2005GL024190.
669 Tolstikhin I., Hofmann A.W., 2005. Early crust on top of the Earth's core. Phys. Earth Planet.
670 Interiors 148, 109–130.
671 Tolstikhin I., O'Nions R., 1996. Some comments on isotopic structure of terrestrial xenon. Chem.
672 Geol. 129, 185–199.
673 Tolstikhin I., Kramers J. D., Hofmann A. W., 2006. A chemical Earth model with whole mantle
674 convection: The importance of a core-mantle boundary layer (D") and its early formation.
675 Chem. Geol., 226, 79-99.
676 Trieloff M., Kunz J., 2005. Isotope systematics of noble gases in the Earth's mantle: possible
677 sources of primordial isotopes and implications for mantle structure. Phys. Earth Planet.
678 Interiors 148, 13–38.
679 Trieloff M., Kunz J., Allègre C. J., 2002. Noble gas systematics of the Reunion mantle plume
680 source and the origin of primordial noble gases in Earth's mantle. Earth Planet. Sci. Lett.
681 200, 297–313.
682 Trieloff M., et al., 2000. The nature of pristine noble gases in mantle plumes. Science 288, 1036.
683 Tucker J. M., Mukhoapdhyay S., Schilling J-G., In press. The heavy noble gas composition of
684 the depleted MORB mantle (DMM) and its implications for the preservation of
685 heterogeneities in the mantle. Earth Planet. Sci. Lett., doi:10.1016/j.epsl.2012.08.025.
686 Turner S., Hawkesworth C., 1998. Using geochemistry to map mantle flow beneath the Lau
687 basin. Geology 26, 1019-1022.

688 Valbracht P.J., et al., 1997. Noble gas systematics of deep rift zone glasses from Loihi Seamount,
689 Hawaii. Earth Planet. Sci. Lett. 150, 399–411.
690 Yatsevich I., Honda M., 1997. Production of nucleogenic neon in the Earth from natural
691 radioactive decay. J. Geophys. Res. **102**, 10291-10298.
692 Yokochi R., Marty B., 2004. A determination of the neon isotopic composition of the deep
693 mantle. Earth Planet. Sci. Lett. 225, 77–88.
694 Yokochi, R., Marty, B., 2005. Geochemical constraints on mantle dynamics in the Hadean. Earth
695 Planet. Sci. Lett. 238, 17–30.

696 **Figure Captions**

697 **Figure 1:** Map showing the location of the four NLD samples along the Rochambeau Rift in the
698 northern Lau back-arc basin.

699 **Figure 2:** Neon three isotope plot for samples from the Rochambeau Rift. Each point represents
700 the Ne isotopic composition of a step crush. Error bars are 1σ. The mantle $^{20}Ne/^{22}Ne$ is set at
701 accretion while $^{21}Ne/^{22}Ne$ evolves as a function of the degree of degassing of a mantle reservoir
702 with low ratios indicative of a less degassed reservoir. Because mantle-derived basalts have
703 vesicles with variable degrees of air contamination, step crushing produces a linear array that lies
704 between air and the mantle composition. Projecting the best fit line through the step crushes to
705 the mantle $^{20}Ne/^{22}Ne$ ratio value yields the mantle $^{21}Ne/^{22}Ne$. While the MORB source has a
706 $^{20}Ne/^{22}Ne$ of 12.5 (Ballentine et al., 2005; Ballentine and Holland, 2008; Raquin et al., 2008), the
707 Iceland and Kola plumes have higher $^{20}Ne/^{22}Ne$, close to the solar composition (Mukhopadhyay,
708 2012; Yokochi and Marty, 2004). We projected the best fit line through the step crushes to the
709 OIB-MORB mixing line, which subsequently defines the mantle source $^{21}Ne/^{22}Ne$ ($^{21}Ne/^{22}Ne_E$)
710 of the basalts. The OIB endmember is based on the least radiogenic $^{21}Ne/^{22}Ne$ measured at
711 Galapagos (Kurz et al., 2009) and the MORB composition is from $^{21}Ne/^{22}Ne$ in depleted MORBs
712 from the equatorial Atlantic (Tucker et al., In press). Best fit lines were calculated using *x* and *y*
713 error weighted fits forced through the atmospheric composition. L2012 is the Ne isotopic data
714 for NLD 13 and NLD 27 from Lupton et al. (2012) and these data are used in calculating the
715 error-weighted best fit lines.

716 **Figure 3.** $^{4}He/^{3}He$ ratios in the Rochambeau Rift samples plotted against the mantle source
717 $^{21}Ne/^{22}Ne$ ratio ($^{21}Ne/^{22}Ne_E$). All of the Rochambeau samples have lower $^{21}Ne/^{22}Ne_E$ compared

718 to the North Altantic popping rock (2ПD43; Moreira et al., 1998) and to depleted MORBs from
719 the Equatorial Atlantic (Tucker et al., In press). The Rochambeau samples appear to show a
720 similar trend to the five Samoan xenoliths from Savai and PPT seamount (Poreda and Farley,
721 1992), but have a higher $^{21}Ne/^{22}Ne_E$ compared to basalts from the Samoan islands of Ofu and
722 Tau (Jackson et al., 2009). The OIB endmember is based on lowest measured $^{4}He/^{3}He$ ratio at
723 Baffin Island (Stuart et al., 2003) and the least nucleogenic $^{21}Ne/^{22}Ne$ from Galapagos (Kurz et
724 al., 2009). The depleted mantle composition was selected based on the extrapolation of the trend
725 observed in depleted MORBs from the equatorial Atlantic (Tucker et al., In press) to a $^{4}He/^{3}He$
726 ratio of 73,000, which corresponds to the He isotopic composition in the most depleted MORBs
727 from the Garret fracture zone (see Mahoney et al., 1993, discussion in Graham et al. 2001). R =
728 $(^{3}He/^{22}Ne)_{MORB}/(^{3}He/^{22}Ne)_{plume}$. For reference, the fields for Galapagos (Kurz et al., 2009),
729 Iceland (Moreira et al., 2001; Mukhoapdhyay 2012; Trieloff et al., 2000), Loihi (Honda et al.,
730 1993; Valbracht et al., 1997), and Manus basin (Shaw et al., 2001) are shown.

731 **Figure 4. A)** Ne-Ar compositions of individual step crushes for the NLD 27 sample from the
732 Rochambeau Rift. ^{40}Ar is generated by radioactive decay of ^{40}K and low $^{40}Ar/^{36}Ar$ ratios are
733 indicative of a less degassed mantle. Popping rock from the North Mid-Atlantic Ridge is shown
734 for comparison (Moreira et al., 1998) and the Bravo Dome well gas data is from Holland and
735 Ballentine (2006). The vesicle compositions in basaltic glass are a combination of magmatic
736 gases and shallow-level post-eruptive air contamination. Step crushing leads to sampling of
737 vesicles with varying degrees of air contamination, which in Ne-Ar space should lead to a
738 hyperbolic trend. A least-squares hyperbolic fit through the data indicate that the mantle source
739 for NLD 27 (Rochambeau source) has a $^{40}Ar/^{36}Ar$ of 16,763 ± 1,144 for a mantle $^{20}Ne/^{22}Ne$ of
740 13.22 (see text for discussion). **B)** Step crushes from samples NLD 13 and NLD 14. The

741 hyperbolic best fit regression for NLD 27 is overlain on the data. The $^{40}Ar/^{36}Ar$ ratios for the
742 NLD 13 and NLD 14 mantle sources appear to be comparable to that of NLD 27.

743 **Figure 5. A)** Hyperbolic mixing between $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{130}Xe$ for the NLD 27 sample from
744 the Rochambeau Rift. Like for Ne-Ar, step crushing leads to sampling of vesicles with varying
745 degrees of air contamination, which will generate a hyperbolic trend between the atmospheric
746 composition and the mantle composition. The correlation shows scatter, likely reflecting the
747 presence of a second fractionated shallow-level air contaminant. A least squares hyperbolic best-
748 fit curve through the data when projected to a mantle $^{20}Ne/^{22}Ne$ of 13.22 yields a mantle source
749 $^{129}Xe/^{130}Xe$ value of 6.92 ± 0.07, significantly lower than measured values in MORBs but similar
750 to the Iceland source of 6.98 ± 0.07. Note that given the curvature in Ar-Xe space, the defined
751 $^{129}Xe/^{130}Xe$ in the Rochambeau mantle source is not particularly sensitive to the exact choice of
752 the mantle $^{40}Ar/^{36}Ar$ ratio. **B**) Step crushes showing the Ar-Xe relation for NLD 13 and NLD 14.
753 The hyperbolic best fit regression for NLD 27 is overlain on the data.

754 **Figure 6.** Elemental abundance ratios plotted against radiogenic isotope ratios for NLD 27
755 (Rochambeau Rift), DICE 10 (Iceland), Galapagos plume and popping rock (MORB). **A)**
756 $^{3}He/^{36}Ar$ vs. $^{40}Ar/^{36}Ar$ and **B)** $^{3}He/^{130}Xe$ vs. $^{129}Xe/^{130}Xe$. Iceland data is from Mukhopadhyay
757 (2012), and the Galapagos data is from Raquin and Moreira (2009), and the popping rock data is
758 from Moreira et al. (1998). Good linear relationships are observed between isotope ratios and
759 elemental ratios, which reflect mixing between mantle-derived noble gases and post-eruptive
760 atmospheric contamination. Note that both the Rochambeau and Iceland plumes define the same
761 trend but are quite distinct from popping rock (MORB source). The mixing lines denote the
762 trajectory along which the mantle source will evolve towards the air composition as subducted
763 air is mixed into the mantle source. Therefore, the low $^{40}Ar/^{36}Ar$ and low $^{129}Xe/^{130}Xe$ ratios in

764 plumes cannot be generated by adding subducted air. Hence, (at least) two distinct mantle
765 reservoirs with different $^{129}Xe/^{130}Xe$ ratios are required. Since ^{129}Xe is produced from ^{129}I decay,
766 the $^{129}Xe/^{130}Xe$ ratio stopped evolving after ^{129}I became extinct 100 Myr after the start of the
767 solar system. As a result, the difference in MORB and plume $^{129}Xe/^{130}Xe$ ratio must have been
768 set up early and the timescale of last major equilibration between the two reservoirs must predate
769 4.45 Ga.

770 **Figure 7**. **A)** Differences in measured $^{129}Xe/^{132}Xe$-$^{136}Xe/^{132}Xe$ between plumes (Iceland and
771 Rochambeau) and depleted MORBs (equatorial Atlantic; Tucker et al., In press). Step crushes in
772 MORBs define a slope of 0.3898 ± 0.0081 (MSWD=0.78) while the plume data define a slope of
773 0.2937 ± 0.0065 (MSWD=0.68). Thus, the depleted MORBs and the Rochambeau and Iceland
774 plumes sources have clear differences in the proportion of radiogenic to fissiogenic Xe; the
775 MORB and plume sources cannot be related to each other solely through recycling of
776 atmospheric Xe. **B)** Differences in measured $^{129}Xe/^{136}Xe$ between the two plumes (Iceland and
777 Rochambeau) and MORBs from the Southwest Indian Ridge (n=104; Parai et al., In revision)
778 and depleted MORBs from the equatorial Atlantic (n=25; Tucker et al., In press). RR ALL stands
779 for the error-weighted average derived from all the step crushes on the NLD 13, NLD 14 and
780 NLD 27 (n= 67; Supplemental Table 2). The measured values have not been corrected for post-
781 eruptive air contamination. However, both post-eruptive contamination and recycling of
782 atmospheric Xe will move the mantle source composition linearly towards the atmospheric
783 composition. Therefore, the small Xe isotopic difference between the Rochambeau-Iceland
784 plumes and MORBs cannot be related solely through recycling atmospheric Xe or by adding
785 fissiogenic ^{136}Xe to MORB Xe.