

# Isotope systematics of Li, Sr, Nd, and volatiles in Indian Ocean MORBs of the Rodrigues Triple Junction: Constraints on the origin of the DUPAL anomaly

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Received 2 May 2006; accepted in revised form 6 October 2006

## Abstract

The DUPAL anomaly, a radiogenic isotope anomaly discovered in the Indian Ocean mantle, has been interpreted as due to a large-scale mantle heterogeneity. To provide new constraints on the DUPAL origin, we analyzed isotope ratios of Li, Sr, and Nd in fresh N-MORB glasses recovered from the Rodrigues Triple Junction in the Indian Ocean, and from the North Atlantic. The Li isotopic compositions of the Indian Ocean DUPAL N-MORBs were comparable to those of the North Atlantic non-DUPAL N-MORBs. The source of the DUPAL signature in Indian Ocean MORBs and the E-MORB-type enriched mantle source have quite different Li isotopic compositions. The  $^{143}\text{Nd}/^{144}\text{Nd}$  values of both sources are significantly lower than those of the North Atlantic N-MORBs. The  $\delta^7\text{Li}$  values of most oceanic island basalts with similar low  $^{143}\text{Nd}/^{144}\text{Nd}$  signatures are also higher than those of the North Atlantic N-MORBs, except for several Koolau lavas. The Li isotope results support the recent proposal that significant amounts of recycled lower continental crust might produce the radiogenic isotope signatures of the Indian Ocean DUPAL source.

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## 1. Introduction

Indian Ocean MORBs typically have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and lower  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  than North Atlantic (N-Atlantic) and East Pacific (E-Pacific) MORBs, and these isotopic characteristics of Indian Ocean MORBs are representative of the DUPAL anomaly (e.g., Dupre et al., 1981; Hart, 1984). Previous studies using Sr, Nd, and Pb isotope tracers (e.g., Rehkamper and Hofmann, 1997 and references therein) considered the DUPAL signature to result from contamination by recycled continental lithosphere, either old subcontinental lithosphere or sediments associated with subducting oceanic crust. Alternatively, the lower continental crust (LCC) may be the source of the DUPAL signature of Indian Ocean MORBs,

as suggested by new Hf and Os isotope results (Escrib et al., 2004; Hanan et al., 2004).

Lithium is an alkali metal trace element that is moderately incompatible during mantle melting (e.g., Brenan et al., 1998). It is a fluid-mobile element, which is a univalent cation ( $\text{Li}^+$ ) in solution, and it provides information different from that provided by well-known radiogenic isotope tracers such as Sr, Nd, and Pb. Lithium has two stable isotopes,  $^7\text{Li}$  and  $^6\text{Li}$ , with abundances of 92.5% and 7.5%, respectively. The large difference in mass between these two isotopes leads to high levels of isotopic fractionation during near-surface processes. Thus, Li abundance and isotope ratios have been used as tracers for near-surface subducted material in the mantle. Subducted components ( $\delta^7\text{Li} < +14\text{‰}$ ) such as altered oceanic crust (Chan et al., 2002) and marine sediments (Chan and Kastner, 2000) have a heavier Li isotopic signature than the mantle ( $\delta^7\text{Li} = +3\text{‰}$ , this study), where  $\delta^7\text{Li} = \left[ \frac{^7\text{Li}}{^6\text{Li}} \right]_{\text{sample}} /$

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$[\text{}^7\text{Li}/\text{}^6\text{Li}]_{\text{L-SVEC standard}} - 1] \times 1000$ . During subduction, substantial Li isotopic fractionation between dehydrated fluid and the residual slab occurs: the  $\delta^7\text{Li}$  value of Li in dehydrated fluid is expected to be higher than that of residual slab Li (Zack et al., 2003). Zack et al. (2003) based their model on dramatically low  $\delta^7\text{Li}$  values ( $-11\text{‰}$  to  $+5\text{‰}$ ) in eclogites from Trescolmen, Switzerland.

As the Li isotope ratio is not affected by time, or by parent–daughter fractionation, it can provide information about the DUPAL anomaly to complement that from radiogenic isotope tracers. We analyzed Li isotope ratios of fresh zero-age Indian Ocean and N-Atlantic MORBs. Reports of Li isotope data from fresh MORBs (Chan et al., 1992; Moriguti and Nakamura, 1998; Tomascak and Langmuir, 1999; Nishio et al., 2002; Elliott et al., 2003) do not always adequately describe the freshness and chemical composition of the MORBs. The freshness of MORB samples is crucial because their  $\delta^7\text{Li}$  values tend to increase because of the uptake over time of heavy Li isotopes from seawater (Chan et al., 1992, 2002). Knowledge of the chemical composition of analyzed MORBs is also crucial to assess the DUPAL signature, because the  $\delta^7\text{Li}$  values of MORBs increase with  $^{87}\text{Sr}/^{86}\text{Sr}$  and La/Sm ratios, and decrease with  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios (Elliott et al., 2003, 2004).

## 2. Samples

All samples used in this study were from fresh glass portions of the chilled margins of deep-sea lavas (water depth, 2500–4100 m). Abundant volatiles are preserved in quenched glass because it forms under high hydraulic pressure and cools rapidly; therefore, quenched glass portions of lavas are commonly used for studies of mantle volatiles (e.g., Marty and Ozima, 1986; Nishio et al., 1998; Nishio et al., 1999). Marginal glasses are also ideal samples of abyssal lava for the study of elements sensitive to seawater alteration (e.g., Sr and Li), because fresh marginal glass is the least altered portion.

Samples were collected from the Indian Ridge near the Rodrigues Triple Junction (RTJ) (25.6°S, 70.0°E). Sample locations and a bathymetric map of the RTJ area have previously been published (Nishio et al., 1999). At the RTJ, three ridges with different spreading rates meet: the Central Indian Ridge (CIR), the Southeast Indian Ridge (SEIR), and the Southwest Indian Ridge (SWIR). The samples analyzed in this study were dredged at stations KH93-3-DR1 (CIR adjacent to RTJ), KH93-3-DR3 (CIR adjacent to RTJ), KH93-3-DR6 (SEIR adjacent to RTJ), KH93-3-DR9 (immediate area of RTJ), and KH93-3-DR25 (immediate area of RTJ) during the KH93-3 cruise of the R/V *Hakuho Maru* (Ocean Research Institute, University of Tokyo). We also analyzed samples of N-Atlantic mid-oceanic ridge lava glasses: 224-R-01 (26.1°N, 44.8°W), CH98-DR11 (30.7°N, 41.8°W), and CH31-DR11 (36.8°N, 33.3°W). Sample 224-R-01 was recovered from the Trans-Atlantic Geotraverse (TAG) hydrothermal mound area (Rona et al., 1986) by the submersible *Shinkai 6500*,

JAMSTEC (Fujioka et al., 1995). Both CH98-DR11 (Bougault and Treuil, 1980) and CH31-DR11 (Bougault and Hekinian, 1974) were dredged samples.

We also analyzed Loihi glasses to identify  $\delta^7\text{Li}$  values of a high  $^3\text{He}/^4\text{He}$  mantle source. The Loihi Seamount, south of the Big Island of Hawaii, is the youngest expression of hot-spot volcanism in the Hawaiian–Emperor chain (Moore et al., 1982). The Loihi Seamount is mainly covered by talus, and there is a ridge in its south rift zone (Valbracht et al., 1997), where samples KH85-4-DE55-1 (along the ridge) and KH85-4-DE54-025 (east slope of the ridge) were dredged during the KH85-4 cruise of the R/V *Hakuho Maru*.

Except for the TAG sample and the two Loihi samples, major elemental compositions and volatile data (C, N, He, and Ar) have been reported previously (Nishio et al., 1998, 1999; Sano et al., 1998). Noble gas data, including Ne, Kr, and Xe, of several studied samples are also available (Hiyagon et al., 1992; Kumagai and Kaneoka, 2003, 2005). Kumagai and Kaneoka (2003) reported the relationship between textures and the noble gas signatures of the studied RTJ Indian Ridge samples.

## 3. Analytical procedure

Fresh glass fragments, without oxidation haloes, from the chilled margins of deep-sea lava blocks were handpicked after repeated crushing. Collected glass fragments were washed ultrasonically in a 5%  $\text{HNO}_3$  solution (15 min) and then cleaned consecutively in distilled water, ethanol, and acetone (15 min each). A weak  $\text{HNO}_3$  solution was used to avoid Li isotopic fractionation during washing (Nishio et al., 2004, 2005). The  $\delta^7\text{Li}$  values of standard samples (SRM 612 50  $\mu\text{g g}^{-1}$  Trace Element Glass standard) with and without leaching in 5%  $\text{HNO}_3$  solution ( $+31.7\text{‰}$  and  $+32.4\text{‰}$ , respectively) agreed within analytical errors and suggest that the observed Li isotopic ratios were not significantly affected by 15 min of leaching with  $\text{HNO}_3$  solution.

The isotopic and elemental compositions of  $\text{CO}_2$ ,  $\text{N}_2$ , He, and Ar in vesicle gas from marginal glasses were first analyzed using the vacuum crushing technique. The detailed procedures for volatile analysis are described by Takahata et al. (1998) and Nishio et al. (1999). The crushed residue was subsequently finely ground in an agate mortar. After digestion of the powdered samples (0.05 g) by concentrated HF and  $\text{HClO}_4$ , the resulting solution was divided into two aliquots: one for measurement of Li–Sr–Nd isotopic ratios and the other for measurement of trace elemental abundances. After column separation using cation exchange resin AG 50W-X8 (Bio-Rad Laboratories Inc.) and Ln resin (Eichrom Technologies Inc.), Li, Sr, and Nd isotopic ratios were determined in solutions with about 100 ng  $\text{g}^{-1}$  Li, 100 ng  $\text{g}^{-1}$  Sr, and 50 ng  $\text{g}^{-1}$  Nd, respectively, using a MC-ICP-MS Isoprobe (GV Instruments Inc, previously Micromass). Samples were introduced into the spectrometer via an Aridus desolvating unit (Cetac Technologies). A T1H nebulizer (Cetac Technologies) was used for Li isotope measurements, whereas a micromist nebulizer

(Glass Expansion Pty Ltd) was used for Sr and Nd isotope measurements. Procedural blanks for Li, Sr, and Nd isotope analyses were less than 10 pg, 50 pg, and 10 pg, respectively. The Li standard solution (NIST L-SVEC) was measured before and after sample analyses to correct for instrumental mass bias in the Li isotope measurements. The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  data were normalized to  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710258$  for SRM987, and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.5121067$  for JNdi-1. The  $\delta^7\text{Li}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $^{143}\text{Nd}/^{144}\text{Nd}$  values we obtained for standard volcanic rocks agreed well (within statistical errors) with previously published data ( $\delta^7\text{Li} = \pm 0.83\text{‰}$ ;  $^{87}\text{Sr}/^{86}\text{Sr} = \pm 0.00006$ ;  $^{143}\text{Nd}/^{144}\text{Nd} = \pm 0.000027$ , 2SD) (Nishio and Nakai, 2002; Nishio et al., 2004). Details of the Li–Sr–Nd isotopic analytical protocols we used have been documented previously (Nishio and Nakai, 2002; Nishio et al., 2004, 2005). Li abundance was determined by MC-ICP-MS after column separation (Nishio and Nakai, 2002). Analytical errors for Li abundances were better than 12% (2RSD), as estimated from the reproducibility of standard rocks (Nishio and Nakai, 2002). Other trace elemental abundances were determined with a quadrupole ICP-MS (PQ3, Thermo Elemental), without purification, and with the matrix effect corrected by using internal standards of indium and rhenium. The major elemental abundances of lava glass samples (other than sample KH85-4-DE54-025, which was too small) were determined by XRF (PW1480, Philips Co.) using portions of powdered samples (0.4 g) (Yoshida and Takahashi, 1997). Sample KH85-4-DE54-025 was analyzed with a broad beam (15  $\mu\text{m}$  diameter) EPMA (JXA-8900RL, JEOL Ltd).

## 4. Results

Isotopic compositions of Li, Sr, Nd, He, Ar, C, and N in the lava samples are listed in Table 1, together with other useful indices. All trace element analyses are provided in Appendix 1, together with reference rock data and reproducibilities. All analyses for major elements and volatiles of the TAG sample and two Loihi samples are listed in Appendix 2; those of the other samples studied have been reported previously (Nishio et al., 1998; Sano et al., 1998; Nishio et al., 1999).

The  $\text{SiO}_2$  and  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  concentrations and the chondrite-normalized  $(\text{La}/\text{Sm})_n$  values indicate that all the mid-oceanic ridge samples we studied were N-MORBs (Table 1). Michard et al. (1986) reported that all of the Indian Ocean MORBs that they recovered from the RTJ area were N-MORBs (Fig. 1a and b). The  $^3\text{He}/^4\text{He}$  ( $\text{R}/\text{R}_A$ ) and  $^{40}\text{Ar}/^{36}\text{Ar}$  values of the studied MORBs varied from 8.0 to 9.0 and from 515 to 19000, respectively (Table 1). Values of  $^3\text{He}/^4\text{He}$  of around 8  $\text{R}/\text{R}_A$  (e.g., Hilton et al., 1993) and those of high  $^{40}\text{Ar}/^{36}\text{Ar}$  (Burnard et al., 1997) are characteristic of fresh MORB glasses. The  $\delta^7\text{Li}$  values of N-MORB glasses obtained in this study (+2.4‰ to +4.1‰) cover a narrower range than those of previous studies (+1.5‰ to +6.5‰) (Chan et al., 1992; Moriguti and Nakamura, 1998; Tomascak and Langmuir, 1999; Elliott et al., 2003). The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios

of the RTJ N-MORBs are, respectively, higher and lower than those of the N-Atlantic N-MORBs (Fig. 1c). The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  values observed in this study (Fig. 1a–c) agree well with previous results for RTJ N-MORBs recovered from the same area (25.2–25.8°S, 69.9–70.2°E) (Michard et al., 1986; Price et al., 1986). In contrast to Sr–Nd isotopic data, no significant difference in Li isotopic composition was observed between RTJ N-MORBs (+2.4‰ to +4.1‰) and N-Atlantic N-MORBs (+2.7‰ to +3.4‰) (Table 1).

The  $^3\text{He}/^4\text{He}$  ratios (25  $\text{R}/\text{R}_A$  and 30  $\text{R}/\text{R}_A$ ) and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios (490 and 669) of the studied Loihi basalt glasses were, respectively, higher and lower than the MORB values (Table 1). The  $(\text{La}/\text{Sm})_n$  values for the Loihi samples ranged from 1.6 to 1.8, and were significantly higher than those of the N-MORBs (Table 1). The  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7036) and  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51295–0.51296) values of the Loihi samples were, respectively, higher and lower than the obtained N-MORB values (Table 1). The  $\delta^7\text{Li}$  values of the Loihi glasses (+4.1‰ and +5.5‰) were higher than the average N-MORB value ( $+3.2 \pm 1.3\text{‰}$ , 2SD) obtained in this study (Table 1).

## 5. Discussion

### 5.1. Seawater alteration

The  $\delta^7\text{Li}$  values observed in the N-MORBs fell within a narrow range from +2.4‰ to +4.1‰, while the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios varied greatly from 515 to 19000 (Fig. 2). Thus, the results of this study showed that pristine  $\delta^7\text{Li}$  values can be observed in MORB glasses with  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios higher than 515. Using Li isotopic results from altered MORBs, Chan et al. (1992) estimated the alteration  $\delta^7\text{Li}$  end-member value to be +14‰. Using this value, the expected Li–Ar isotope shift of N-MORBs as a result of progressive seawater alteration is shown in Fig. 2.

Potassium/rubidium ratios have been proposed as an index of progressive seawater alteration of abyssal basalts (Hart, 1969; Verma, 1992). The  $\delta^7\text{Li}$  values observed in the N-MORBs fell within a narrow range from +2.4‰ to +4.1‰, while the K/Rb ratios varied from 350 to 740. Accordingly, our results indicated that pristine  $\delta^7\text{Li}$  values can be observed in MORBs with K/Rb ratios between 350 and 740.

### 5.2. The DUPAL signature of the RTJ N-MORBs

#### 5.2.1. Sr, Nd, and Li isotopes

The expected Sr–Nd isotope shifts of N-Atlantic MORBs as a result of progressive seawater alteration were estimated from the results of binary mixing between N-Atlantic MORBs and seawater (Fig. 1c) (end-member values used for the mixing calculation are in Appendix 3). This plot demonstrates that the Sr and Nd isotopic differences between Indian Ocean and N-Atlantic MORBs cannot be explained by seawater alteration.

Table 1  
Li–Sr–Nd–He–Ar–C–N isotopic compositions and key indices of marginal glasses of pillow lavas from the RTJ Indian Ocean and North Atlantic mid-oceanic ridges and the south rift zone of Loihi Seamount, Hawaii

Sample	Indian Ridges (Triple Junction area)					North Atlantic Ridge			Seamount (Hawaii)		[Uncertainty] <sup>a</sup>
	KH93-3-DR3-A1	KH93-3-DR1-F1	KH93-3-DR9-G1	KH93-3-DR25-A1	KH93-3-DR6-A1	224-R-01	CH98-DR11	CH31-DR11	KH85-4-DE54-025	KH85-4-DE55-1	
Site <sup>b</sup>	CIR	CIR	RTJ	RTJ	SEIR	NAR (TAG)	NAR	NAR	Loihi (east slope of S. rift)	Loihi (on S. rift)	
Latitude	25.23°S	25.37°S	25.50°S	25.58°S	25.80°S	26.14°N	30.68°N	36.83°N	18.82°N	18.80°N	
Longitude	69.92°E	70.03°E	70.07°E	70.07°E	70.22°E	44.83°W	41.82°W	32.25°W	155.20°W	155.20°W	
Depth (m)	4090	4030	4080	4270	3640	3646	3600	2480	3260	3180	
$\delta^7\text{Li}$ (‰)	+4.1	+2.5	+4.0	+2.4	+3.0	+3.4	+3.2	+2.7	+5.5	+4.1	[±0.83‰, 2SD]
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70309	0.70307	0.70310	0.70313	0.70318	0.70255	0.70254	0.70281	0.70363	0.70356	[±0.00006, 2SD]
$^{143}\text{Nd}/^{144}\text{Nd}$	0.513043	0.513040	0.513087	0.513079	0.513049	0.513187	0.513212	0.513186	0.512962	0.512953	[±0.000027, 2SD]
$^3\text{He}/^4\text{He}$ (R/R <sub>A</sub> )	8.47 <sup>d</sup>	8.13 <sup>d</sup>	7.96 <sup>d</sup>	8.42 <sup>d</sup>	8.55 <sup>d</sup>	8.46	8.97 <sup>d</sup>	8.64 <sup>d</sup>	30.4	25.3	[±10%, 2RSD]
$^{40}\text{Ar}/^{36}\text{Ar}$	3150 <sup>e</sup>	515 <sup>d</sup>	11,300 <sup>d</sup>	17,000 <sup>e</sup>	4950 <sup>e</sup>	6760	19,000 <sup>e</sup>	5190 <sup>e</sup>	490	669	
[2SD] <sup>c</sup>	±130	±15	±1300	±4000	±320	±580	±12,000	±890	±13	±16	
$\delta^{13}\text{C}$ (‰) of CO <sub>2</sub>	−2.59 <sup>d</sup>	−2.99 <sup>d</sup>	−5.58 <sup>d</sup>	−3.12 <sup>d</sup>	−3.95 <sup>d</sup>	−2.77	−3.10 <sup>d</sup>	−5.72 <sup>d</sup>	−1.36	−1.90	[±0.2‰, 2SD]
$\delta^{15}\text{N}$ (‰) of N <sub>2</sub>	−1.7 <sup>e</sup>	−2.2 <sup>d</sup>	−1.0 <sup>d</sup>	−2.3 <sup>e</sup>	−2.0 <sup>e</sup>	−3.2	−3.1 <sup>e</sup>	−1.2 <sup>e</sup>	+0.5	+0.4	[±1‰, 2SD]
SiO <sub>2</sub> (wt%)	49.6 <sup>d</sup>	50.1 <sup>d</sup>	50.4 <sup>d</sup>	51.0 <sup>d</sup>	49.9 <sup>d</sup>	49.9	49.6 <sup>d</sup>	50.2 <sup>d</sup>	46.3	46.9	[±0.6%, 2RSD]
Na <sub>2</sub> O (wt%)	2.79 <sup>d</sup>	3.08 <sup>d</sup>	2.92 <sup>d</sup>	2.76 <sup>d</sup>	3.06 <sup>d</sup>	2.82	2.50 <sup>d</sup>	2.53 <sup>d</sup>	2.29	2.56	[±1.3%, 2RSD]
K <sub>2</sub> O (wt%)	0.03 <sup>d</sup>	0.15 <sup>d</sup>	0.06 <sup>d</sup>	0.03 <sup>d</sup>	0.05 <sup>d</sup>	0.08	0.03 <sup>d</sup>	0.11 <sup>d</sup>	0.78	0.57	[±0.8%, 2RSD]
[weight ratios] <sup>f</sup>											
Li/Yb	2.34	2.03	2.00	2.38	2.16	1.87	1.87	1.86	2.96	3.16	[±17%, 2RSD]
Li/Y	0.263	0.226	0.225	0.244	0.240	0.205	0.213	0.215	0.260	0.277	[±14%, 2RSD]
K/Rb	558	741	545	606	483	721	402	347	646	512	[±5%, 2RSD]
(La/Sm) <sub>n</sub> <sup>g</sup>	0.51	0.81	0.60	0.54	0.59	0.59	0.51	0.84	1.8	1.6	[±12%, 2RSD]
(La/Yb) <sub>n</sub> <sup>g</sup>	0.60	0.91	0.62	0.63	0.68	0.70	0.54	0.89	6.5	5.6	[±14%, 2RSD]
(Sm/Yb) <sub>n</sub> <sup>g</sup>	1.2	1.1	1.0	1.2	1.1	1.2	1.0	1.1	3.6	3.4	[±16%, 2RSD]
[mole ratios]											
$^4\text{He}/^{40}\text{Ar}^*$	3.9 <sup>d</sup>	19 <sup>d</sup>	6.6 <sup>d</sup>	3.7 <sup>d</sup>	3.6 <sup>d</sup>	13	6.8 <sup>d</sup>	12 <sup>d</sup>	1.3	1.4	[±14%, 2RSD]
CO <sub>2</sub> / <sup>3</sup> He (×10 <sup>9</sup> )	0.39 <sup>d</sup>	0.35 <sup>d</sup>	0.33 <sup>d</sup>	0.20 <sup>d</sup>	0.55 <sup>d</sup>	0.51	1.58 <sup>d</sup>	1.92 <sup>d</sup>	2.54	2.17	[±37%, 2RSD]

<sup>a</sup> Uncertainty has been estimated by reproducibility (2SD) of repeated measurement of standard material.

<sup>b</sup> CIR, Central Indian Ridge; RTJ, immediate area of Rodrigues Triple Junction; SEIR, Southeast Indian Ridge; NAR, North Atlantic Ridge; TAG, Trans-Atlantic Geotraverse; S. rift, South rift zone of Loihi seamount.

<sup>c</sup> Internal errors that are standard deviation (2SD) of acquired  $^{40}\text{Ar}/^{36}\text{Ar}$  data within a run of the measurement.

<sup>d</sup> Data have been already reported in Nishio et al. (1999).

<sup>e</sup> Data have been already reported in Sano et al. (1998).

<sup>f</sup> Full data sets of the trace elemental abundances are listed in Appendix 1.

<sup>g</sup> CI chondrite-normalized La/Sm, La/Yb, and Sm/Yb ratios. La, Sm, and Yb abundances of the CI chondrite are from McDonough and Sun (1995).

It is also clear that the enriched Sr and Nd isotopic signatures of the RTJ MORBs are not due to an E-MORB-type enriched mantle source, because of the similarity of the La/Sm ratios of the Indian Ocean and N-Atlantic MORBs (Fig. 1a and b). The large-scale mantle heterogeneity known as the DUPAL anomaly has been expressed by Hart (1984) in terms of  $\Delta 7/4\text{Pb}$  and  $\Delta 8/4\text{Pb}$ , and defined as the vertical deviation from the Northern Hemisphere Reference Line (NHRL). Significantly high  $\Delta 7/4\text{Pb}$  (+6 to +12) and  $\Delta 8/4\text{Pb}$  (+69 to +78) values have been observed in RTJ N-MORBs with enriched Sr and Nd isotope signatures (Michard et al., 1986; Price et al., 1986). Consequently, we also attributed the enriched Sr and Nd isotope signatures that we observed in the RTJ MORBs to DUPAL contamination of the source, not to seawater alteration and/or the presence of an E-MORB-type enriched mantle source.

In contrast to the Sr and Nd isotope results, no systematic difference was observed in  $\delta^7\text{Li}$  values between the RTJ N-MORBs ( $+3.2 \pm 1.6\text{‰}$ , 2SD) and the N-Atlantic N-MORBs ( $+3.1 \pm 0.7\text{‰}$ , 2SD). The  $\delta^7\text{Li}$  values were not shifted by isotope fractionation due to crystal-melt reactions, because no systematic difference was observed in the differentiation indices, such as  $\text{SiO}_2$  content (Table 1). Tomascak et al. (1999) also has suggested that Li isotope fractionation at the per mil level does not occur during high-temperature processes.

### 5.2.2. Li/Yb ratio

Ryan and Langmuir (1987) suggested that, because of the constant Li/Yb and Li/Y ratios of MORBs, the mineral-melt partitioning behavior of Li during melting and fractional crystallization closely resembles that of Yb and Y. Thus, to separate the effects of differentiation (crystal-melt equilibrium) from other Li-additional processes, Li/Yb and Li/Y ratios have been used as indicators of excess Li-enrichment of lavas (e.g., Moriguti and Nakamura, 1998; Chan et al., 1999).

The Li/Yb values of DUPAL N-MORBs ( $\Delta 7/4\text{Pb} \geq 2.5$ ;  $\Delta 8/4\text{Pb} \geq 15$ ) tend to be higher than those of non-DUPAL N-MORBs ( $\Delta 7/4\text{Pb} < 2.5$ ;  $\Delta 8/4\text{Pb} < 15$ ) (Fig. 3a and b, Appendices 4 and 5). The Li/Yb ratios of the RTJ N-MORBs (2.00–2.38) tend to be higher than those of the N-Atlantic N-MORBs (1.86–1.87). However, no difference was observed in differentiation indices such as  $\text{SiO}_2$  content and  $(\text{La}/\text{Sm})_n$ ,  $(\text{La}/\text{Yb})_n$ , and  $(\text{Sm}/\text{Yb})_n$  ratios between the Indian Ocean and N-Atlantic MORBs (Table 1). Among these differentiation indices, La/Yb and Sm/Yb ratios provide information on garnet-bearing differentiation, because HREEs such as Yb and Y are more compatible in garnet than Li and LREEs such as La or Sm. Consequently, the observed difference in Li/Yb values between Indian Ocean and N-Atlantic MORBs cannot be attributed to differentiation (including garnet-bearing differentiation).

### 5.3. Li isotope systematics of lavas having enriched Sr–Nd isotope signatures

Elliott et al. (2003) reported that  $\delta^7\text{Li}$  values of E-Pacific MORBs increased from +3.1‰ to +5.2‰ with decreasing

$^{143}\text{Nd}/^{144}\text{Nd}$  ratios from 0.51325 to 0.51315. The increasing  $\delta^7\text{Li}$  values observed in E-Pacific MORBs have been attributed to an E-MORB-type enriched mantle source because the  $\delta^7\text{Li}$  values also correlate positively with La/Sm ratios (Elliott et al., 2003, 2004). Comparison of the Li–Nd isotope trend of MORBs from the E-Pacific (Elliott et al., 2003, 2004) with data of this study (Fig. 4a) shows that the source of the DUPAL signature in Indian Ocean MORBs and the E-MORB-type enriched mantle source have quite different  $\delta^7\text{Li}$  signatures of +3‰ and >+5‰, respectively, (Elliott et al., 2003, 2004) (Fig. 4a).

Comparison of Li–Nd and Li–Sr isotopic correlations of the Loihi glasses of this study with previously reported oceanic island basalt (OIB) data (Fig. 4a and b) (Chan and Frey, 2003; Ryan and Kyle, 2004; Nishio et al., 2005) showed  $\delta^7\text{Li}$  values of +4.1‰ and +5.5‰ for the two Loihi glasses with high  $^3\text{He}/^4\text{He}$  ratios ( $>25 \text{ R/R}_A$ ). These  $\delta^7\text{Li}$  values are significantly higher than those of the N-Atlantic MORBs (+3.1‰). The whole-rock  $\delta^7\text{Li}$  values of many OIBs from Mangaia, Tubuai Rurutu, Tahiti, Hiva Oa, Ua Pou (Polynesia), and Marie Byrd Land (Antarctica) are also higher than the N-Atlantic N-MORB value (+3‰). In contrast, the  $\delta^7\text{Li}$  values of several Koolau (Hawaii) OIBs are significantly lower than those of other OIBs with similarly enriched Sr–Nd isotopic compositions (Chan and Frey, 2003) (Fig. 4a and b).

Based on Sr, Nd, and Pb radiogenic isotopic data, four end-member geochemical reservoirs have been proposed as the source of OIBs: depleted mantle (DM), high  $^{238}\text{U}/^{204}\text{Pb}$  mantle (HIMU), and two types of enriched mantle (EM1 and EM2) (e.g., Zindler and Hart, 1986). From N-Atlantic non-DUPAL N-MORB data obtained in this study, we estimated  $+3.1 \pm 0.7\text{‰}$  (2SD) as the  $\delta^7\text{Li}$  value of the DM end-member component. Relative to this DM value, the higher  $\delta^7\text{Li}$  values of both HIMU (+5‰ to +7‰) and EM2 (>+6‰) end-member components have been reported from Polynesian OIB data (Nishio et al., 2005).

As mentioned above, the  $\delta^7\text{Li}$  values of several Koolau OIBs are lower than those of other OIBs that are related to HIMU and EM2 components (Chan and Frey, 2003). Because the low  $^{206}\text{Pb}/^{204}\text{Pb}$  values (17.8–17.9) of the Koolau OIBs (Roden et al., 1994) indicate the involvement of an EM1 component in their source, together with other end-member components, Nishio et al. (2004) attributed the lower  $\delta^7\text{Li}$  values of the Koolau OIBs to the EM1 end-member component. Nishio et al. (2004) further inferred a low  $\delta^7\text{Li}$  value of the EM1 end-member value ( $>-17\text{‰}$ ), based on the results of mantle-derived ultramafic xenoliths. However, a definitive  $\delta^7\text{Li}$  value of the EM1 end-member has not been determined owing to a lack of data from EM1-dominant OIBs such as Pitcairn lavas.

Based on radiogenic isotopic signatures, the involvement of an EM1 end-member component, together with an EM2 end-member component, in the Indian Ocean DUPAL source has been proposed (e.g., Agranier et al., 2005). Thus, we inferred that the relatively low  $\delta^7\text{Li}$  values of the

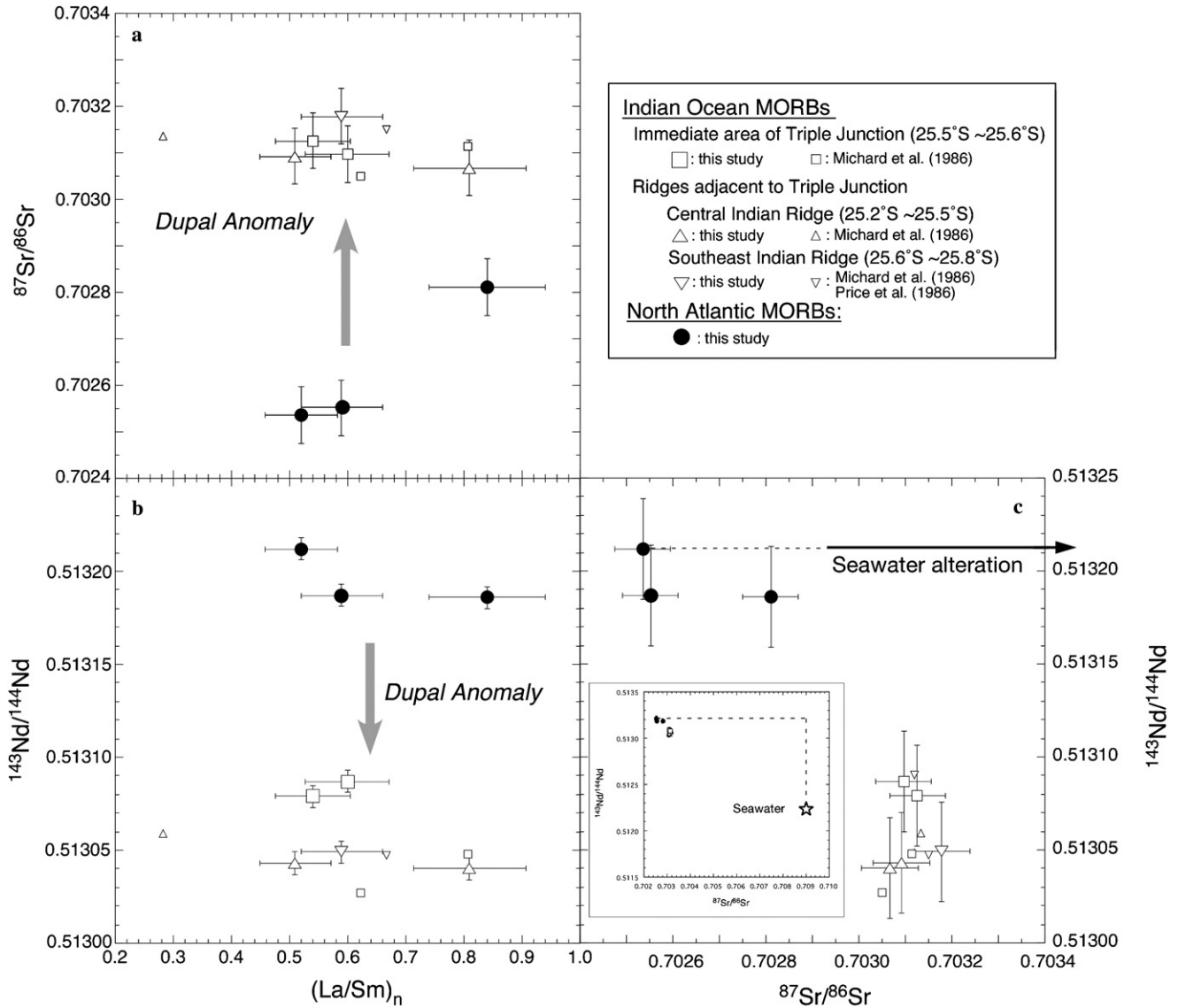


Fig. 1. Correlations of  $(\text{La}/\text{Sm})_n$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  (a),  $(\text{La}/\text{Sm})_n$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  (b), and  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  (c) of RTJ MORBs and N-Atlantic MORBs. Previous results for RTJ MORBs recovered from the same area as this study (25.2–25.8°S; 69.9–70.2°E) (Michard et al., 1986; Price et al., 1986) are also shown. Errors shown are listed in Table 1. The expected Sr–Nd isotope shift of the N-Atlantic N-MORBs because of progressive seawater alteration is shown as the dashed line in figure (c), and is estimated from the results of binary mixing of N-Atlantic N-MORBs and Indian Ocean deep seawater. End-member values used for the mixing calculation are listed in Appendix 3.

Indian Ocean DUPAL N-MORBs and several Koolau OIBs can be attributed to the EM1 reservoir.

#### 5.4. Cause of the DUPAL signature in Indian Ocean MORBs

##### 5.4.1. Recycled sediment

The  $\text{C}/^3\text{He}$  ratio has been used as a sensitive indicator of recycled carbon in volcanic gases (e.g., Marty and Jambon, 1987; Sano and Marty, 1995; Sano and Williams, 1996). Kingsley and Schilling (1995) observed that  $\text{C}/^3\text{He}$  values for vesicle-derived gases of the N-Atlantic MORB samples tend to increase with decreasing  $^{143}\text{Nd}/^{144}\text{Nd}$  values (Fig. 5), which they interpreted to reflect a contribution from a recycled C-rich component associated with the

Azores plume. Available data for less degassed MORB samples identified by  $^4\text{He}/^{40}\text{Ar}^*$  values of  $\leq 30$  are also shown in the  $^{143}\text{Nd}/^{144}\text{Nd}$ – $\text{C}/^3\text{He}$  ( $\approx \text{CO}_2/^3\text{He}$ ) diagram (Fig. 5). The  $^4\text{He}/^{40}\text{Ar}^*$  value is a good index of the degree of fractional degassing, because the He and Ar solubilities differ by a factor of 10. It is also likely that the  $\text{CO}_2/^3\text{He}$  values of relatively less degassed MORB samples ( $^4\text{He}/^{40}\text{Ar}^* \leq 30$ ) should be approximately equal to the  $\text{CO}_2/^3\text{He}$  value of a pristine magma source, based on the results of calculations using the  $\text{CO}_2$ –He–Ar solubilities (Marty and Tolstikhin, 1998; Marty and Zimmermann, 1999). The  $^{143}\text{Nd}/^{144}\text{Nd}$ – $\text{C}/^3\text{He}$  data distribution of the Indian Ocean MORBs is quite different from those of the N-Atlantic and E-Pacific MORBs (Fig. 5). Furthermore, the  $^{143}\text{Nd}/^{144}\text{Nd}$ – $\text{C}/^3\text{He}$  data distribution suggests that the source of the DUPAL signature

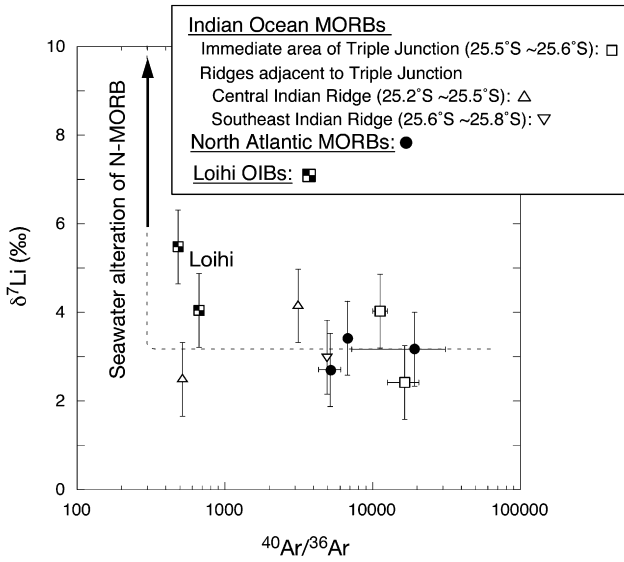


Fig. 2. Correlation of  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $\delta^7\text{Li}$  for the N-MORBs and Loihi OIBs. Errors shown are listed in Table 1. The expected Li–Ar isotope shift of N-MORBs because of progressive seawater alteration is shown as a dashed line.

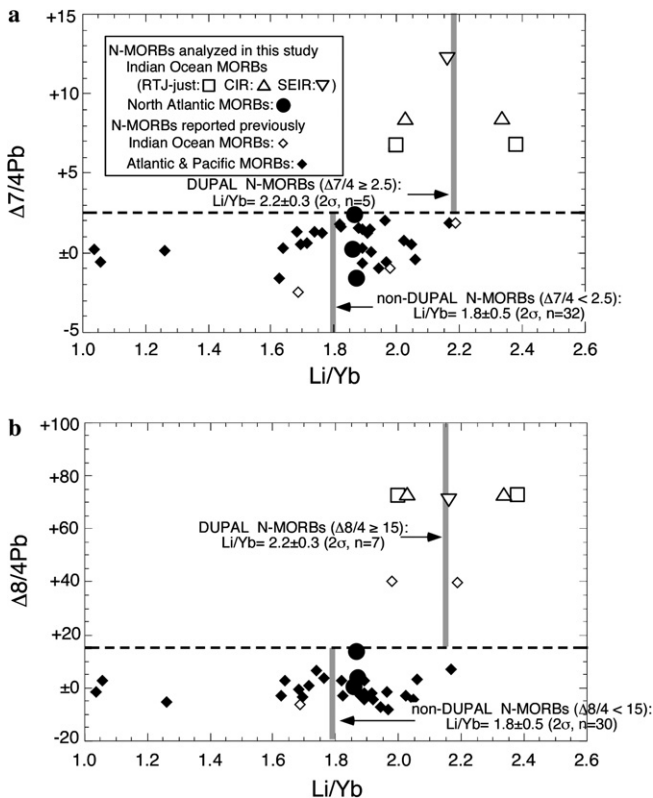


Fig. 3. Li/Yb weight ratios as a function of  $\Delta 7/4\text{Pb}$  (a) and  $\Delta 8/4\text{Pb}$  (b) of N-MORBs [ $\text{SiO}_2 = 45\text{--}52\text{ wt}\%$ ;  $(\text{La}/\text{Sm})_n < 1$ ]. The Pb isotopic composition of North Atlantic MORB sample CH98-DR11 has been previously reported (Hamelin et al., 1984). Because the Pb isotopic compositions of other MORB samples have not been documented, we estimated the  $\Delta 7/4\text{Pb}$  and  $\Delta 8/4\text{Pb}$  values of the sampling area from available N-MORB data (Appendix 4). These diagrams also show data from other N-MORBs whose  $\text{SiO}_2$ , Li, Yb, La, and Sm contents, and Pb isotopic compositions are available (Appendix 5).

in Indian Ocean MORBs and the E-MORB-type enriched mantle source have quite different  $C^3\text{He}$  values, which are, respectively, low ( $< 1 \times 10^9$ ) and high ( $\sim 4 \times 10^9$ ). Consequently, subducted sedimentary carbon with high  $C^3\text{He}$  can be definitively rejected as the source of the Indian Ocean DUPAL signature.

#### 5.4.2. Lower continental crust (LCC)

Hanan et al. (2004) reported that Indian Ocean DUPAL MORBs showing high  $\Delta 8/4\text{Pb}$  values have positive  $\Delta \epsilon_{\text{Hf}}$  values (+8 to +1), which are significantly higher than those of non-DUPAL MORBs (+1 to –5). The  $\Delta \epsilon_{\text{Hf}}$  value is defined as the vertical deviation from the  $\epsilon_{\text{Nd}}\text{--}\epsilon_{\text{Hf}}$  mantle array. The anomalously high  $\Delta \epsilon_{\text{Hf}}$  values of the Indian Ocean DUPAL MORBs require a time-integrated Lu/Hf source composition substantially different from that of all other known oceanic basalt mantle sources, including those of both MORB and OIB. Based on these Hf isotopic results, Hanan et al. (2004) argued that a LCC possibly caused the DUPAL anomaly in Indian Ocean MORBs. Furthermore, Escrig et al. (2004) demonstrated that significant amounts of LCC melt are required to produce the Os–Pb–Sr–Nd isotopic composition of Indian Ocean DUPAL-type MORBs.

The  $\delta^7\text{Li}$  and Yb/Li values of MORBs analyzed in this study are shown in Fig. 6 together with DM and LCC end-member values (Rudnick and Gao, 2003; Teng et al., 2004). The  $\delta^7\text{Li}$  value of the DM end-member was estimated as +3.1‰ from the average of the N-Atlantic N-MORB data obtained in our study. The Yb/Li value of the DM was estimated to be 0.56 (Li/Yb = 1.8) from the average of the non-DUPAL N-MORBs with  $\Delta 8/4\text{Pb}$  values lower than 15 (Fig. 3b). The  $\delta^7\text{Li}$  and Yb/Li values of LCC have been estimated to be +1‰ and 0.12 (Li/Yb = 8.7), respectively, from high-grade metamorphic terrane and granulite-facies xenolith data (Rudnick and Gao, 2003; Teng et al., 2004). Using these end-member values, the  $\delta^7\text{Li}$  and Yb/Li values of the RTJ N-MORBs can be explained by binary mixing of DM and LCC components (Fig. 6). In this case, about 20% of Li in RTJ MORBs can be attributed to recycled LCC. Our estimation using Li data agrees with a previous estimation using the radiogenic isotope compositions of Os, Pb, Sr, and Nd (Escrig et al., 2004): Escrig et al. (2004) proposed that about 10% of the melt should be derived from LCC in order to produce the Os–Pb–Sr–Nd isotopic compositions of RTJ MORBs. During the melting process, mafic rocks are expected to be more fertile than the peridotitic mantle, and thus to melt to a higher degree, so that their contribution in the liquid phase is increased by a factor of three to four compared with the pristine solid mafic–ultramafic proportions (Hirschmann and Stolper, 1996). Taking this effect into consideration, Escrig et al. (2004) further pointed out that the DUPAL signature of RTJ MORBs requires less than 4% of LCC to be added to its source. Thus, the Li isotope data support the previous proposal that significant amounts of recycled LCC are probably the cause of the Indian Ocean DUPAL signature.

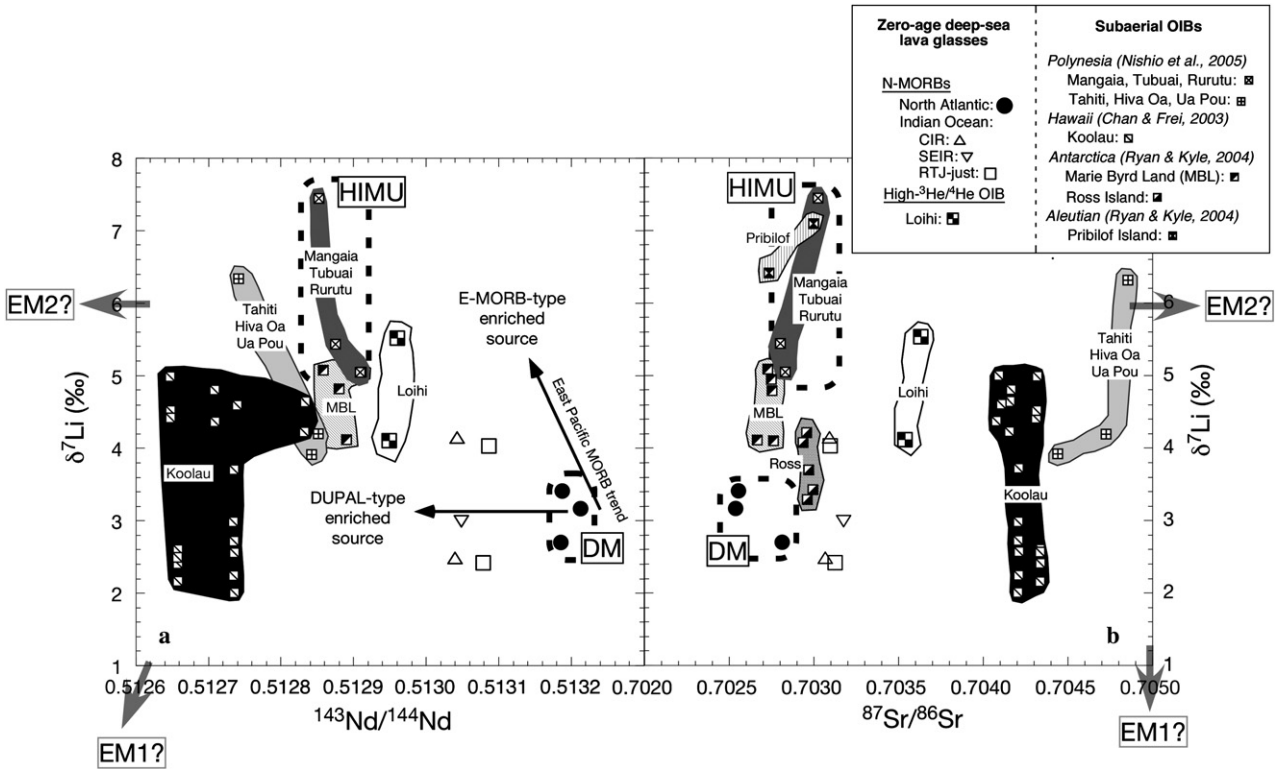


Fig. 4.  $\delta^7\text{Li}$  values as a function of the  $^{143}\text{Nd}/^{144}\text{Nd}$  (a) and  $^{87}\text{Sr}/^{86}\text{Sr}$  (b) of MORBs and OIBs. MORB and Loihi OIB glass data were determined in this study. Subaerial OIB data are from the following papers: Polynesia [Mangaia, Tubuai, Rurutu, Tahiti, Hiva Oa, and Ua Pou] (Nishio et al., 2005); Hawaii [Koolau] (Chan and Frey, 2003); Antarctica [Marie Byrd Land and Ross Island] and the Aleutian Islands [Pribilof Island] (Ryan and Kyle, 2004). The Nd and Sr isotopic compositions of the mantle reservoirs (DM, HIMU, EM1, and EM2) are from Zindler and Hart (1986). The  $\delta^7\text{Li}$  value of the DM reservoir was estimated from the N-Atlantic N-MORB data determined in this study. The  $\delta^7\text{Li}$  value of the HIMU reservoir was estimated from HIMU OIB data (Nishio et al., 2005). The  $\delta^7\text{Li}$  values of the EM1 and EM2 reservoirs were estimated from mantle-derived xenolith data (Nishio et al., 2004).

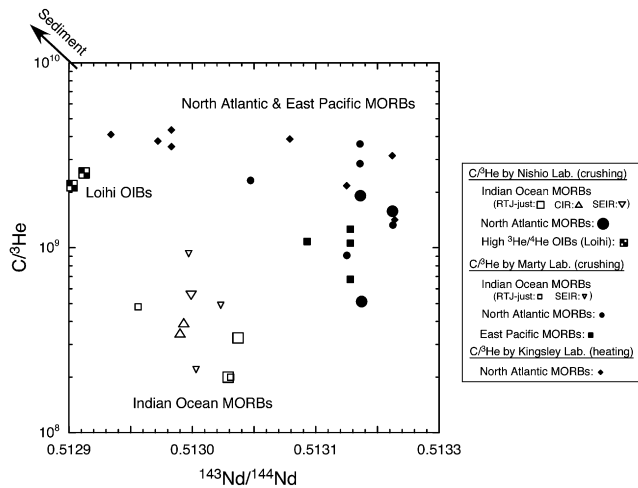


Fig. 5. Correlation of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios and  $\text{C}^3\text{He}$  mole ratios of MORB glasses from N-Atlantic, E-Pacific, and Indian Ocean. The  $\text{C}^3\text{He}$  values in this figure were determined by three separate laboratories: Kingsley Lab (Kingsley and Schilling, 1995), Marty Lab. (Marty and Tolstikhin, 1998; Marty and Zimmermann, 1999), and Nishio Lab. (this study and 1999). The  $\text{C}^3\text{He}$  values of Kingsley Lab were estimated from vesicle- $\text{C}^3\text{He}$  values determined using the stepwise heating technique, while the  $\text{C}^3\text{He}$  values of the Marty and Nishio Labs were estimated from vesicle- $\text{CO}_2^3\text{He}$  values determined using the crushing technique. The data shown are from the relatively less degassed samples ( $^4\text{He}/^{40}\text{Ar}^* \leq 30$ ) only, except for the data from the Kingsley Lab, for which  $^4\text{He}/^{40}\text{Ar}^*$  is unknown (Kingsley and Schilling, 1995). The  $^{143}\text{Nd}/^{144}\text{Nd}$  data sources are listed in Appendix 6.

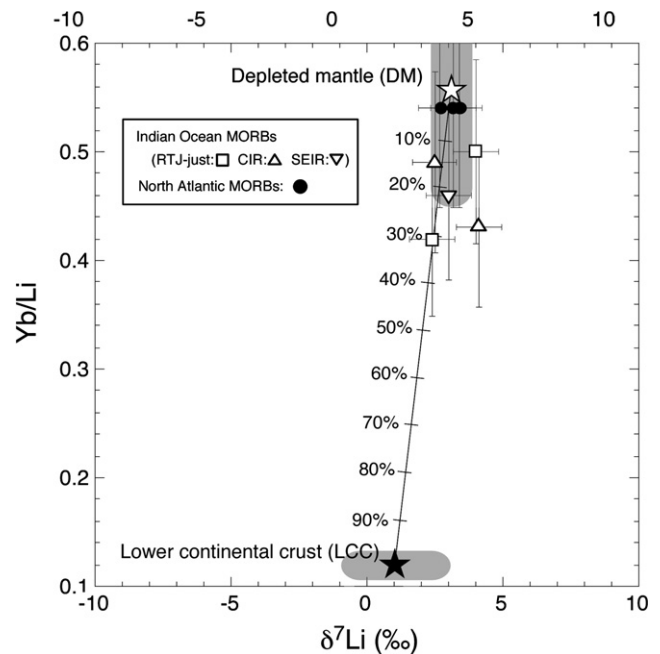


Fig. 6. Correlation of  $\delta^7\text{Li}$  values and Yb/Li weight ratios of MORB glasses. Solid line indicates a binary mixing trend between depleted mantle (DM) and lower continental crust (LCC). The  $\delta^7\text{Li}$  and Li/Yb values of the DM and LCC sources are explained in the text. Errors shown are listed in Table 1.

## 6. Conclusions

No systematic Li isotopic difference was observed between the RTJ DUPAL N-MORBs ( $+3.2 \pm 1.6\%$ , 2SD) and the N-Atlantic non-DUPAL N-MORBs ( $+3.1 \pm 0.7\%$ , 2SD). Thus, the source of the DUPAL signature in Indian Ocean MORBs and the source of E-MORB-type enriched mantle have quite different  $\delta^7\text{Li}$  values, which are  $+3\%$  and  $>+5\%$ , respectively (Elliott et al., 2003). The  $^{143}\text{Nd}/^{144}\text{Nd}$  values of both sources are lower than those of the North Atlantic N-MORBs. The  $\delta^7\text{Li}$  values of most OIBs related to HIMU and/or EM2 sources are also higher than that of DM ( $+3\%$ ) (Chan and Frey, 2003; Ryan and Kyle, 2004; Nishio et al., 2005). In contrast, the  $\delta^7\text{Li}$  values of several Koolau OIBs are significantly lower than those of other OIBs with low  $^{143}\text{Nd}/^{144}\text{Nd}$  signature (Chan and Frey, 2003). Thus, we inferred that the relatively low  $\delta^7\text{Li}$  values of the Indian Ocean DUPAL N-MORBs and several Koolau OIBs can be attributed to an EM1 reservoir.

Based on the Hf isotopic results, Hanan et al. (2004) argued that LCC was a possible cause of the DUPAL anomaly in Indian Ocean MORBs. Our Li isotope results can be explained by a model in which significant amounts of recycled LCC produce the DUPAL isotopic signatures of the Indian Ocean MORB source.

## Acknowledgments

This manuscript benefited from thoughtful and constructive reviews and improvements in English expression by Marissa Tejada. We are grateful to Harue Masuda (TAG samples) and Hajime Hiyagon (CH31–CH98 samples) for providing the N-Atlantic MORB samples, and Toshitaka Gamo for providing the Loihi samples. We also thank W. Soh and staff of the Kochi Core Center who have made every effort to provide an excellent research environment for Y. Nishio. Special thanks to K. Sato, H. Yamaguchi, M. Sakaguchi, and N. Takahata for their help with analyses of major and volatile elements, respectively. Comments from T. Matsumoto, J. Yamamoto, M. Handler, H. Amakawa, T. Hanyu, H. Kumagai, T. Ishikawa, and K. Suzuki are also gratefully acknowledged. We thank Y. Tatsumi and S. Nakada for supporting this work. The “Petrological Database of the Ocean Floor (PETDB, <http://www.petdb.org/>)” was used for obtaining previously reported abyssal glass data. This study was supported by the following grants: a Grant-in-Aid for Scientific Research to Y. Nishio (No. 16740309) and H. Kumagai (No. 14540457) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Reviews by Bernard Marty, Jon Snow, Paul Tomascak, and an anonymous referee helped to clarify the presentation and are greatly appreciated.

Associate editor: Bernard Marty

## Appendix 1

Trace elemental abundances of studied marginal glasses of pillow lavas from the mid-oceanic ridge and the southern rift zone of Loihi Seamount, Hawaii

Sample	Indian Ridges (Triple Junction area)					North Atlantic Ridge			Seamount (Hawaii)		Reference Data	
	KH93-3-DR3-A1	KH93-3-DR1-F1	KH93-3-DR9-G1	KH93-3-DR25-A1	KH93-3-DR6-A1	224-R-01	CH98-DR11	CH31-DR11	KH85-4-DE54-025	KH85-4-DE55-1	JB-1a	(2RSD) <sup>a</sup>
<i>Li abundance (<math>\mu\text{g g}^{-1}</math>) determined by MC-ICP-MS after Li-purification</i>												
Li	6.76	5.59	7.63	6.24	5.60	6.14	6.73	6.32	4.65	5.65	10.6	(12%)
<i>Other trace element abundances (<math>\mu\text{g g}^{-1}</math>) determined by quadruple ICP-MS without purification</i>												
Rb	0.45	1.63	0.87	0.48	0.89	0.88	0.70	2.58	10.0	9.27	10.4	(5%)
Sr	112	140	96.6	97.8	120	111	92.8	96.4	324	373	241	(9%)
Y	25.7	24.8	33.9	25.6	23.4	29.9	31.5	29.4	17.9	20.4	24.7	(7%)
Ba	7.46	17.7	11.4	6.12	13.3	9.09	11.2	31.3	133	139	274	(5%)
La	2.54	3.69	3.49	2.45	2.59	3.40	2.84	4.44	15.1	14.6	4.90	(7%)
Ce	8.43	10.7	11.4	7.96	8.21	10.3	9.17	11.6	30.3	34.2	12.5	(7%)
Pr	1.50	1.79	1.98	1.44	1.40	1.82	1.63	1.90	4.77	4.60	2.01	(9%)
Nd	8.30	8.85	10.8	7.73	7.77	10.0	9.28	9.78	18.8	22.2	10.1	(7%)
Sm	3.08	2.85	3.63	2.83	2.72	3.57	3.44	3.30	5.23	5.61	3.17	(10%)
Eu	1.16	1.16	1.40	1.10	1.05	1.31	1.34	1.28	1.79	1.97	1.11	(13%)
Gd	4.09	3.79	5.31	3.70	3.29	4.72	4.65	4.24	4.79	5.78	3.74	(6%)
Tb	0.75	0.73	0.96	0.73	0.65	0.89	0.95	0.85	0.88	0.90	0.72	(8%)
Dy	5.04	4.70	6.20	4.72	4.40	5.68	6.23	5.58	4.35	4.85	4.44	(7%)
Ho	1.09	0.97	1.37	1.00	0.92	1.24	1.36	1.18	0.79	0.86	0.99	(6%)
Er	3.20	2.86	4.05	3.15	2.52	3.69	3.93	3.42	1.82	2.19	2.83	(8%)
Tm	0.45	0.44	0.62	0.44	0.41	0.53	0.59	0.51	0.28	0.29	0.43	(11%)
Yb	2.89	2.76	3.82	2.63	2.59	3.29	3.61	3.40	1.57	1.79	2.73	(12%)
Lu	0.39	0.41	0.51	0.40	0.37	0.49	0.57	0.52	0.25	0.27	0.43	(11%)

<sup>a</sup> Relative standard deviation ( $2\sigma$ ) of repeated measurements of JA-1 (Li,  $n = 5$ ; other elements,  $n = 7$ ).

## Appendix 2

Volatile data (C–N–He–Ar) of vesicle-gas and the chemical compositions of marginal glasses of pillow lavas from the North Atlantic TAG and the Loihi

Sample	224-R-01	KH85-4-DE54-025	KH85-4-DE55-1
<i>Volatile data</i>			
Crushing 1 (for He isotopic data)			
Sample weight (g)	1.24	0.35	2.42
<i>Isotopic ratios</i>			
$^3\text{He}/^4\text{He}$ (R/R <sub>A</sub> ) <sup>a</sup>	8.46	30.4	24.6
<i>Concentrations</i>			
$^4\text{He}$ ( $\times 10^{-10}$ mol/g)	6.3	0.18	0.96
Crushing 2 (for C–N–Ar data)			
Sample weight (g)	2.76	0.82	1.66
<i>Isotopic ratios</i>			
$^{40}\text{Ar}/^{36}\text{Ar}$	6760	490	669
$\delta^{13}\text{C}$ (‰) of CO <sub>2</sub>	–2.77	–1.36	–1.90
$\delta^{15}\text{N}$ (‰) of N <sub>2</sub>	–3.2	+0.5	+0.4
<i>Concentrations</i>			
CO <sub>2</sub> ( $\times 10^{-6}$ mol/g)	1.88	5.73	8.09
N <sub>2</sub> ( $\times 10^{-9}$ mol/g)	2.8	8.6	11.1
$^4\text{He}$ ( $\times 10^{-10}$ mol/g)	3.1	0.53	1.06
$^{40}\text{Ar}$ ( $\times 10^{-11}$ mol/g)	2.5	10.7	13.6
<i>Major elemental abundances<sup>b</sup></i>			
SiO <sub>2</sub>	49.6	46.3	46.9
Al <sub>2</sub> O <sub>3</sub>	14.9	13.4	12.7
TiO <sub>2</sub>	1.63	3.41	2.96
Fe <sub>2</sub> O <sub>3</sub>	11.0	11.6	13.2
MnO	0.18	0.19	0.18
MgO	8.77	6.39	7.86
CaO	11.1	11.7	12.2
Na <sub>2</sub> O	2.82	2.29	2.56
K <sub>2</sub> O	0.08	0.78	0.57
P <sub>2</sub> O <sub>5</sub>	0.16	nd	0.30
Total	100.6	95.97	99.50

<sup>a</sup> Sample  $^3\text{He}/^4\text{He}$  ratios are normalized to the atmospheric  $^3\text{He}/^4\text{He}$  ratio,  $R_A = 1.4 \times 10^{-6}$ . The  $^3\text{He}/^4\text{He}$  ratios listed in this table were measured by a noble gas mass spectrometer (6-60-SGA, Nuclide CO.) without separating He from Ne. It has, however, been reported that there is a systematic difference of 8.9% in the  $^3\text{He}/^4\text{He}$  ratios between Nuclide and VG5400 instruments which is possibly caused by Ne interference on He isotope measurements (Sano et al., 1998). Then, the  $^3\text{He}/^4\text{He}$  ratios obtained by 6-60-SGA are corrected for the difference of analytical system (Nishio et al., 1999).

<sup>b</sup> 224-R-001 and KH85-4-DE55-1 data were determined by XRF. KH85-4-DE54-025 data were determined by EPMA. The listed EPMA data is the average of 10 spot data. (nd, data were not determined).

## Appendix 3

End-member values on the binary mixing calculation shown in Fig. 1c

	Deep seawater (Indian Ocean)	MORB (North Atlantic)
$^{87}\text{Sr}/^{86}\text{Sr}$	0.709 <sup>a</sup>	0.7025 <sup>d</sup>
Sr (mol g <sup>-1</sup> )	$9.1 \times 10^{-8}$ <sup>b</sup>	$1.2 \times 10^{-6}$ <sup>c</sup>
$^{143}\text{Nd}/^{144}\text{Nd}$	0.51223 <sup>c</sup>	0.51321 <sup>e</sup>
Nd (mol g <sup>-1</sup> )	$2.5 \times 10^{-14}$ <sup>c</sup>	$6.3 \times 10^{-8}$ <sup>f</sup>

<sup>a</sup> Data from Palmer and Edmond (1989).

<sup>b</sup> Data from Bruland and Lohan (2003).

<sup>c</sup> Data from Goldstein and Hemming (2003).

<sup>d</sup> The lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  of North Atlantic MORBs analyzed in this study.

<sup>e</sup> Average values of North Atlantic MORBs analyzed in this study.

<sup>f</sup> The highest  $^{143}\text{Nd}/^{144}\text{Nd}$  of North Atlantic MORBs analyzed in this study.

## Appendix 4

Sample ID (this study)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\Delta 7/4\text{Pb}$	$\Delta 8/4\text{Pb}$	References (sample ID)
<i>Sample whose Pb isotopes have already been reported</i>						
CH98-DR11	18.084	15.476	37.627	2.5	13.6	Hamelin et al. (1984) (CHR0098-011)
<i>Samples whose Pb isotopes have never been reported (Pb isotopes were estimated from reported adjacent MORB data)</i>						
KH93-3-DR3-A1	17.316	15.452	37.290	8.4	72.8	Michard et al. (1986) (DUF0023-003-001)
KH93-3-DR1-F1	17.316	15.452	37.290	8.4	72.8	Michard et al. (1986) (DUF0023-003-001)
KH93-3-DR9-G1	17.488	15.455	37.500	6.8	73.0	Michard et al. (1986) (CHRRODR-3-003-001)
KH93-3-DR25-A1	17.488	15.455	37.500	6.8	73.0	Michard et al. (1986) (CHRRODR-3-003-001)
KH93-3-DR6-A1	17.661	15.528	37.697	12.3	71.8	Price et al. (1986) (AII0093-6-013-001)
224-R-01	18.123	15.440	37.579	-1.6	4.1	Hamelin et al. (1984) (CHR0098-015)
CH31-DR11	18.790	15.530	38.350	0.2	0.6	Dupre et al. (1981) (ARP1974-007-005C)

Appendix 5

Sample ID	SiO <sub>2</sub> (wt%)	MgO (wt%)	<sup>87</sup> Sr/ <sup>86</sup> Sr	<sup>143</sup> Nd/ <sup>144</sup> Nd	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb	Δ7/ 4Pb	Δ8/ 4Pb	(La/ Sm) <sub>n</sub>	(La/ Yb) <sub>n</sub>	(Sm/ Yb) <sub>n</sub>	Li/Y	Li/ Yb	References
<i>North Atlantic MORB</i>															
ALV0534-002-001	50.3	9.91	0.70288	0.513079	18.899	15.545	38.435	0.53	-4.09				0.190		Bryan and Moore (1977), Bryan et al. (1979), Ito et al. (1987)
<i>East Pacific MORBs</i>															
108DR1	50.3	7.80	0.70291	0.513120	18.405	15.492	37.885	0.59	0.64	0.80	0.90	1.13		1.71	Prinzhofer et al. (1989)
108DR4	51.5	7.79	0.70269	0.513159	18.297	15.477	37.774	0.26	2.59	0.70	0.82	1.17		1.64	Prinzhofer et al. (1989)
CYA1982-001-004	50.6	8.49	0.70261	0.513098	18.427	15.502	37.900	1.35	-0.52	0.56	0.61	1.08		1.68	Prinzhofer et al. (1989)
CYA1982-006-001	49.6	8.28	0.70288	0.513118	18.271	15.484	37.753	1.24	3.64	0.38	0.41	1.09	0.165	1.76	Prinzhofer et al. (1989); Hekinian et al., 1989
CYA1982-018-001	49.8	7.53	0.70260	0.513111	18.390	15.487	37.844	0.25	-1.65	0.90	1.11	1.23		1.04	Prinzhofer et al. (1989)
CYA1982-020-002	49.8	8.11	0.70271	0.513120	18.385	15.485	37.801	0.11	-5.35	0.53	0.54	1.01		1.26	Prinzhofer et al., 1989
CYA1982-021-004	50.1	8.60	0.70253	0.513130	18.200	15.460	37.663	-0.39	3.22	0.80	1.15	1.44	0.174	2.06	Prinzhofer et al. (1989), Hekinian et al. (1989)
CYA1982-027-001	50.8	7.64	0.70256	0.513103	18.327	15.491	37.850	1.34	6.57	0.74	1.02	1.37	0.155	1.74	Prinzhofer et al. (1989); Hekinian et al. (1989)
CYA1982-027-002	49.8	7.96	0.70260	0.513137	18.380	15.502	37.918	1.86	6.96	0.75	1.11	1.48	0.186	2.17	Prinzhofer et al. (1989); Hekinian et al. (1989)
CYA1982-027-005	49.8	8.56	0.70274	0.513139	18.294	15.468	37.774	-0.61	2.96	0.93	1.22	1.31		1.06	Prinzhofer et al., 1989
MELPHNX-2-044-002	51.4	5.73	0.70268	0.513157	18.315	15.484	37.738	0.77	-3.18	0.65	0.79	1.21	0.208	2.02	Regelous et al. (1999)
MELPHNX-2-045-001	51.6	3.27	0.70254	0.513159	18.299	15.480	37.718	0.54	-3.25	0.74	0.93	1.25	0.177	1.70	Regelous et al. (1999)
MELPHNX-2-047-003	51.4	5.28	0.70256	0.513152	18.337	15.494	37.769	1.53	-2.74	0.77	0.94	1.23	0.195	1.88	Regelous et al. (1999)
MELPHNX-2-051-005	51.6	5.66	0.70252	0.513167	18.311	15.479	37.723	0.31	-4.20	0.67	0.76	1.14	0.201	1.89	Regelous et al. (1999)
MELPHNX-2-054-003	51.0	6.99	0.70247	0.513180	18.248	15.463	37.607	-0.61	-8.18	0.58	0.66	1.14	0.207	1.97	Regelous et al. (1999)
MELPHNX-2-055-003	50.8	6.31	0.70253	0.513153	18.321	15.467	37.706	-1.00	-7.11	0.64	0.74	1.15	0.202	1.94	Regelous et al. (1999)
MELPHNX-2-056-002	50.8	6.67	0.70255	0.513159	18.322	15.492	37.758	1.49	-2.03	0.66	0.77	1.17	0.200	1.92	Regelous et al. (1999)
MELPHNX-2-060-002	50.3	4.93	0.70253	0.513157	18.296	15.475	37.703	0.07	-4.39	0.68	0.82	1.20	0.198	1.92	Regelous et al. (1999)
MELPHNX-2-062-001	50.5	6.10	0.70254	0.513150	18.321	15.497	37.762	2.00	-1.51	0.69	0.83	1.20	0.204	1.96	Regelous et al. (1999)
MELPHNX-2-063-001	50.7	5.62	0.70255		18.347	15.492	37.779	1.22	-2.95	0.68	0.80	1.17	0.200	1.91	Regelous et al. (1999)
MELPHNX-2-068-001	50.4	6.87	0.70259	0.513167	18.307	15.492	37.732	1.65	-2.82	0.72	0.87	1.21	0.190	1.82	Regelous et al. (1999)
MELPHNX-2-069-002	50.6	6.73	0.70255	0.513156	18.338	15.484	37.754	0.52	-4.36	0.69	0.80	1.16	0.213	2.05	Regelous et al. (1999)
MELPHNX-2-077-006	51.5	5.84	0.70251	0.513173	18.305	15.490	37.737	1.47	-2.07	0.65	0.76	1.17	0.196	1.89	Regelous et al. (1999)
NHOCHEP-003-003	49.5	7.50	0.70256	0.513140	18.295	15.468	37.774	-0.62	2.83			1.12	0.187	1.89	Ryan and Langmuir (1987), Castillo et al. (2000)
NHOCHEP-004-001	50.0	7.04	0.70261	0.513078	18.487	15.513	38.007	1.80	2.92			1.32	0.173	1.82	Ryan and Langmuir (1987), Castillo et al. (2000)
NHOCHEP-026-001	49.7	6.40	0.70255	0.513141	18.368	15.466	37.803	-1.61	-3.09			1.27	0.170	1.63	Ryan and Langmuir (1987), Castillo et al. (2000)
<i>Indian Ocean MORBs</i>															
MOA8801-016-012	50.1	7.79	0.70258	0.513064	18.798	15.504	38.291	-2.47	-6.28	0.94	1.29	1.36	0.176	1.69	Pyle et al. (1992), Danyushevsky et al. (2000)
VEM0033-2-007-003	51.2	7.33	0.70290	0.513037	18.057	15.439	37.858	-0.94	40.01	1.00	1.34	1.34	0.200	1.98	Ryan and Langmuir (1987), Klein et al. (1988), Klein et al. (1991)
VEM0033-2-007-007	49.9	9.11	0.70300	0.513007	18.008	15.462	37.794	1.89	39.53	0.79	1.00	1.27	0.207	2.19	Ryan and Langmuir (1987), Klein et al. (1988), Klein et al. (1991)

## Appendix 6

Sample ID (C–He–Ar data)	$^4\text{He}/^{40}\text{Ar}^*$	$\text{C}/^3\text{He}$ ( $\times 10^9$ )	References of C–He–Ar data	$^{143}\text{Nd}/^{144}\text{Nd}$	References of Nd data (sample ID)
Vesicle- $\text{C}/^3\text{He}$ measured by Marty Lab. (crushing)					
<i>North Atlantic MORBs</i>					
2PD-43	1.2	2.3	Marty and Tolstikhin (1998)	0.513097	Dosso et al. (1991) (ABP1985-043-003)
CH98-11	6.2	1.3	Marty and Tolstikhin (1998)	0.513212	This study (CH98-DR11)
CH98-DR15	4.5	0.91	Marty and Tolstikhin (1998)	0.513175	Chauvel and Blichert-Toft (2001) (CHR0098-015)
CH31-DR11	13	3.7	Marty and Tolstikhin (1998)	0.513186	This study (CH31-DR11)
CH31-DR11 No. 4	19	2.9	Marty and Tolstikhin (1998)	0.513186	This study (CH31-DR11)
<i>East Pacific MORBs</i>					
CL-DR01-5V	15	0.68	Marty and Tolstikhin (1998)	0.513178	Chaussidon et al. (1991) (CHRCLIP-001-005V)
CL-DR01-5V-B	17	1.1	Marty and Tolstikhin (1998)	0.513178	Chaussidon et al. (1991) (CHRCLIP-001-005V)
CL-DR01	21	1.3	Marty and Zimmermann (1999)	0.513178	Chaussidon et al. (1991) (CHRCLIP-001-005V)
NAUDUR-DR21-4	19	1.1	Marty and Zimmermann (1999)	0.513143	Schiano et al. (1997) (NADNAUD-021-004)
<i>Indian Ocean MORBs (Rodrigues Triple Junction)</i>					
JC0300703D1	7.2	0.48	Marty and Zimmermann (1999)	0.513006	Salter (1996) (JC0300703D1)
MD 23 SITE 4	2.2	0.20	Marty and Zimmermann (1999)	0.513081	Salter (1996) (DUF0023-004-004)
MD23 SITE2	5.7	0.93	Marty and Zimmermann (1999)	0.513047	Michard et al. (1986) (DUF0023-002-001)
MD37 05/03 D1	6.0	0.22	Marty and Zimmermann (1999)	0.513053	Hamelin et al. (1986) (DUF0037-003-001)
<i>Indian Ocean MORBs (Southeast Indian Ridge)</i>					
HY09-07H	16	0.49	Marty and Zimmermann (1999)	0.513073	Dosso et al. (1988) (CHRHYAM-009-007)
Vesicle- $\text{C}/^3\text{He}$ measured by Kingsley Lab. (heating)					
<i>North Atlantic MORBs</i>					
TR123-5D		3.2	Kingsley and Schilling (1995)	0.513212	Kingsley and Schilling (1995)
TR123-1D		3.9	Kingsley and Schilling (1995)	0.513129	Kingsley and Schilling (1995)
TR89-30D		4.3	Kingsley and Schilling (1995)	0.513033	Kingsley and Schilling (1995)
TR154-17D		3.5	Kingsley and Schilling (1995)	0.513033	Kingsley and Schilling (1995)
TR154-16D		3.8	Kingsley and Schilling (1995)	0.513022	Kingsley and Schilling (1995)
TR154-14D		4.1	Kingsley and Schilling (1995)	0.512984	Kingsley and Schilling (1995)
TR138-7D		1.4	Kingsley and Schilling (1995)	0.513214	Kingsley and Schilling (1995)
EN025-4D		2.2	Kingsley and Schilling (1995)	0.513175	Kingsley and Schilling (1995)

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