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Lithium isotopes in global mid-ocean ridge basalts

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Abstract

The lithium isotope compositions of 30 well-characterized samples of glassy lavas from the three major mid-ocean ridge segments of the world, spanning a wide range in radiogenic isotope and elemental content and sea floor physical parameters, have been measured. The overall data set shows a significant range in δ^7Li (+1.6 to +5.6), with no global correlation between Li isotopes and other geochemical or tectonic parameters. The samples with the greatest lithophile element depletion (N-MORB: $K_2O/TiO_2 < 0.09$) display an isotopic range consistent with the extant database. Samples with greater trace element enrichment display a greater degree of isotopic variability and trend toward heavier compositions ($\delta^7Li = +2.4$ to +5.6), but are not distinct on average from N-MORB. Together with published data, N-MORB is estimated to have mean $\delta^7Li = +3.4 \pm 1.4\text{‰}$ (2σ), consistent with the estimate for an uncontaminated MORB source based on pristine peridotite xenoliths. Locally, where sampling density permits, sources of Li isotope heterogeneity may be evaluated. Sample sets from the East Pacific Rise show correlation of δ^7Li with halogen concentration ratios. This is interpreted at 15.5°N latitude to represent incorporation of <5 weight percent recycled subduction-modified mantle in the MORB source. At 9.5°N latitude the data are more consistent with shallow level magma chamber contamination by seawater-derived components (<0.5 wt.%).
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1. INTRODUCTION

The strong contrast in Li isotope compositions of the mantle and surface environments of the Earth suggests that this isotope system may be a sensitive tracer of mass transfer between surficial and deep-seated reservoirs. In spite of this, our current understanding of the Li isotope composition of mid-ocean ridge basalt (MORB), the most accessible window into the mantle, is predicated on four analyses of samples from the Atlantic and Pacific Oceans ($\delta^7Li = +3.4$ to +4.7; Chan et al., 1992). This and an earlier study (Chan and Edmond, 1988) were the first to demonstrate the very large difference in Li isotope composition

between mid-ocean ridge basalts and ocean water ($\delta^7Li = c. +31$; Millot et al., 2004). Few additional analyses of MORB samples have since reported similar isotope compositions (Elliott et al., 2006; Moriguti and Nakamura, 1998; Nishio et al., 2007; Tomascak and Langmuir, 1999), with a minority of slightly isotopically lighter and heavier samples. The Li isotope compositions of pristine mantle peridotite xenoliths are relatively restricted ($\delta^7Li = c. +3.5$; Jeffcoate et al., 2007), but it is unclear if this range is representative of the source regions for MORB.

Studies of magmatic arcs generally indicate that the sub-arc mantle has Li isotope compositions that lie within the range measured for MORB (Chan et al., 2002b; Leeman et al., 2004; Tomascak et al., 2000, 2002). However, some interpretations implicate isotopically lighter mantle sources ($\delta^7Li \sim 0$; Moriguti and Nakamura, 1998), although this may instead reflect contributions from melting dehydrated, isotopically fractionated subducted crust (Magna et al., 2006a; Tomascak et al., 2000). The growing database for ocean island basalts (OIB) illustrates a similar average Li

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isotope composition to that accepted for MORB (+4.6; range = +1.4 to +10.4; Chan and Frey, 2003; Jeffcoate et al., 2007; Kobayashi et al., 2004; Nishio et al., 2005; Ryan and Kyle, 2004; Tomascak et al., 1999b). The lack of a systematic study of well-characterized unaltered MORB samples significantly hampers a full evaluation of the nature of Li isotopes in the mantle. This is important to resolve for precisely quantifying the global budget of Li.

The origin of geochemical heterogeneity in MORB has received considerable study. Although an influence from trace element enriched ocean island sources appears likely in some regions (e.g., Schilling et al., 1983; Sun et al., 1979), heterogeneities in other areas are ascribed to the incorporation of recycled components from a veined upper mantle into a depleted bulk (e.g., Dosso et al., 1999; Eiler et al., 2000; Zindler and Hart, 1986). Furthermore, the depleted component does not appear to be globally consistent, leading to isotopic provinciality among the ridge systems (Hamelin et al., 1986). It has not been determined if Li isotopes in MORB show equivalent heterogeneities.

Chan et al. (1992) analyzed samples of glassy MORB and found δ^7Li values ranging from +3.4 to +6.8 (±1.2‰ 2σ). Samples with $K_2O > 0.13$ wt.% had $\delta^7Li > +5$. They interpreted the more K-rich samples as illustrating the effects of subtle seawater alteration, which was supported by petrographic evidence. One sample with 0.16 wt.% K_2O was thus excluded from the set of unaltered MORB. Although the number of samples (six, from which two were excluded) was too small to provide a statistically significant test for the viability of this criterion for seawater alteration, their range for 'fresh' MORB (+3.4 to +4.7) has become the accepted value in the literature.

A global survey of unaltered MORB glass revealed Li concentrations of 2.9–7.8 ppm for samples with at least 6 wt.% MgO (Ryan and Langmuir, 1987). Mid-ocean ridge lavas in the upper several hundred meters of the sea floor take on lithium during low temperature alteration. Alteration reactions progress with duration of exposure to seawater, such that older altered basalts from the Mid-Atlantic ridge have Li contents up to 11 times higher than younger basalts close to the ridge and 14 times unaltered basalts (Chan et al., 1992). Oceanic crust from below 1 km depth is complex in terms of Li isotopes, with both isotopically heavy and light materials relative to unaltered basalt ($\delta^7Li = -1.7$ to +7.9; Chan et al., 2002a), although all of these rocks appear to be depleted in Li (<3 ppm). Investigations of volatile element contents of MORB have suggested that some visibly unaltered samples carry cryptic alteration, in which elemental and isotope systematics are compromised by incorporation of seawater components in the magmatic plumbing system (Michael and Schilling, 1989). As such, a distinction between a magma source isotope signature and magma chamber contamination may be complicated. How well can we rule out such contamination effects at the fine scale, and ultimately to what extent can we use submarine basalts to assess the 'pristine' MORB Li isotope range?

In the current study we have attempted to provide a framework through which these problems may be more systematically addressed by analyzing a group of well-charac-terized MORB samples from sites along ridges in the Atlantic, Pacific and Indian oceans. Although not globally comprehensive in a geographical sense, the samples span a very broad range in composition, and are thus an effective subset of the whole for the purpose of global examination. In order to address the potential problems introduced locally during magma chamber processes we have examined in detail a set of samples from a segment of the East Pacific Rise (EPR), where contamination by a brine-enriched crustal component has been documented with a number of elemental and isotopic systems (le Roux et al., 2006). With these data we demonstrate that some of the heterogeneity in the Li isotope composition of MORB is consistent with high-level contamination processes, and hence is not intrinsic to the mantle.

2. SAMPLES

2.1. Locations

The MOR volcanic rock samples come from three separate ridges that span a wide range of spreading rate and bathymetric character (Fig. 1, Table 1). We have concentrated on basaltic samples for which accompanying data have been published previously. The classification of MORB by bulk chemical composition has used a number of indicators (e.g., K_2O/TiO_2, La/Sm, Ba/TiO_2; Langmuir et al., 1986; Reynolds et al., 1992; Schilling et al., 1983; Sun et al., 1979). In this report we separate samples on the basis of K_2O/TiO_2 because of the more complete compilation of major element data for the global data set as opposed to trace elements. One of the major goals of the study was to compare MORB of "normal" chemical compositions from globally dispersed locations. Of 30 total samples, six are strongly depleted in large-ion lithophile elements, with $K_2O/TiO_2 < 0.09$ and, where data are available, low Ce/Yb and Ba/Y. We refer to these as N-MORB in the text. Nine samples have notable trace element enrichment and $K_2O/TiO_2 > 0.4$. These are some of the characteristic features of E-MORB (Langmuir et al., 1986), although we avoid using this terminology on specific samples owing to the lack of complete trace element data. The remaining 14 samples have compositions intermediate between the aforementioned two classes.

The 12 Mid-Atlantic Ridge (MAR) samples span a range in latitude from 23.1°N to 39.1°N, proximal to and south of the Azores hotspot. All but one of the six samples with $K_2O/TiO_2 > 0.4$ come from a cluster at approximately 35.2°N. Three of the remaining six samples have more intermediate elemental compositions, and the other three have $K_2O/TiO_2 < 0.05$. The MAR samples come from the widest range of depths among the ridge segments analyzed (3731–1386 m below sea level). Some of the MAR samples in this study were previously examined by Dosso et al. (1999), Reynolds and Langmuir (1997), and Shirey et al. (1987).

The three Indian Ridge samples (IR) have intermediate values of K_2O/TiO_2. These samples come from the southeast portion of this ridge, between 115°E and 124°E longitude. Two are from within the Australian–Antarctic
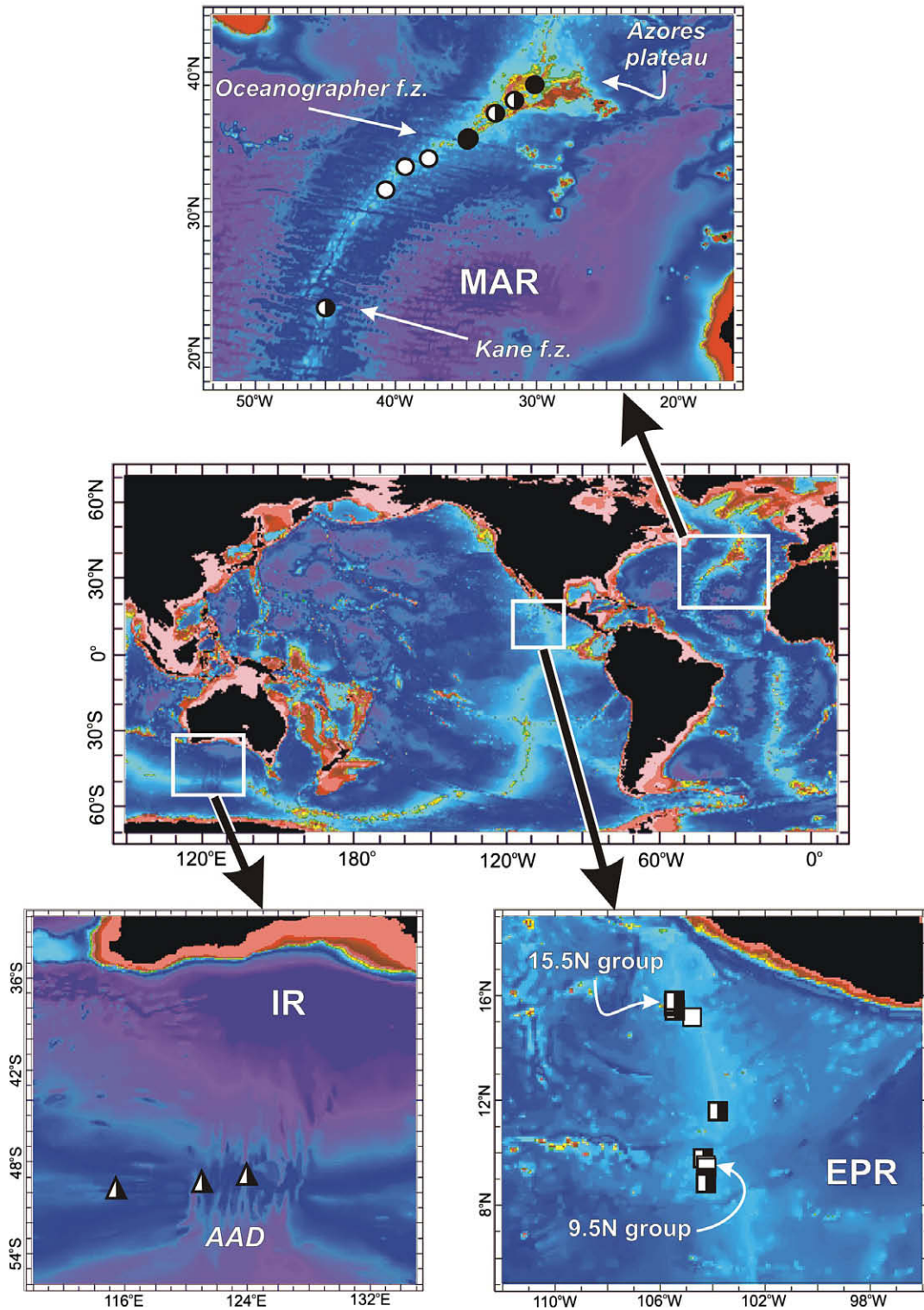
Fig. 1. Location of samples used in this study, plotted using the IRI WORLDBATH topography tool. White symbols are incompatible trace element depleted MORB with K_2O/TiO_2 (wt.%) < 0.09, black symbols have K_2O/TiO_2 > 0.4 and split-color symbols are intermediate between these values. Diagrams that follow use the symbol shapes from these maps to distinguish ridge of origin and the patterns to discriminate elemental compositions.

Discordance (AAD; Fig. 1) where the ridge reaches extreme depth (down to 3989 m below sea level). Some of the IR samples in this study were previously examined by Klein et al. (1988, 1991).

Table 1
Geographical and tectonic data for samples from this study

Sample number	Locality latitude, longitude	Depth (mbsl)	Spreading rate (mm/a)	Type [*]
Mid-Atlantic Ridge				
AII0127-1-022-002	39.038°N, 30.025°W	1386	24	g
AII0127-1-018-002	37.979°N, 31.471°W	1725	21	g
AII0127-1-014-003	37.062°N, 32.888°W	2985	21	g
AII0127-2-044GL	35.326°N, 34.859°W	2396	22	g
AII0127-2-045GL	35.295°N, 34.864°W	2435	22	g
AII0127-1-R018	35.305°N, 34.864°W	2240	22	g
AII0127-2-046-011T3	35.237°N, 34.817°W	2038	22	g
ALV1016-001	35.12°N, 34.95°W	3731	22	r
AII0127-1-005	33.910°N, 37.712°W	3070	22	g
AII0127-1-001	33.174°N, 39.248°W	2706	23	g
OC180 17-3	31.66°N, 40.78°W	2740	23	—
KNO0115-020	23.135°N, 44.983°W	3225	14	g
Indian Ridge				
VEM0033-2-007-007	49.033°S, 124.0°E	3989	75	g
VEM0033-2-008-008	49.467°S, 121.03°E	3532	75	g
VEM0033-2-010-003	49.917°S, 115.375°E	3087	75	g
East Pacific Rise				
VE31-2	15.2°N, 104.83°W	2920	87	—
NHOCHEP-036-001	11.654°N, 103.84°W	2540	100	g
NHOCHEP-087-008	9.440°N, 104.232°W	2584	108	r
NHOCHEP-082-008	9.115°N, 104.198°W	2548	109	g
NHOCHEP-075-001	8.837°N, 104.228°W	2550	110	g
15.5N group:				
D63-1	15.82°N, 105.44°W	2299	84	g
D22-1	15.71°N, 105.43°W	2314	84	g
D29-5	15.59°N, 105.40°W	2325	85	g
D30-A	15.47°N, 105.38°W	2348	85	g
D30-B	15.47°N, 105.38°W	2348	85	g
D30-C	15.47°N, 105.38°W	2348	85	g
9.5N group:				
ALV2759-005	9.82°N, 104.31°W	2665	106	g
ALV2489-008	9.53°N, 104.21°W	2934	108	g
ALV2489-009	9.53°N, 104.21°W	2917	108	g
AII0125-24-R032-D	9.51°N, 104.22°W	2704	108	g

Note. —, data not available; spreading rates calculated using the algorithm from. http://www.ldeo.columbia.edu/~menke/plates.html.
[*] Sample type: r, bulk rock; g, hand-picked glass.

Fifteen samples from the Pacific span a section of the East Pacific Rise (EPR) from 8.8°N to 15.8°N latitude, with clusters of samples around 9.5°N and 15.5°N. Four of the samples have $K_2O/TiO_2 < 0.09$. Neither of the two samples with $K_2O/TiO_2 > 0.4$ are basalts (63.0 and 67.5 wt.% SiO_2, 1.90 and 1.38 wt.% K_2O, respectively), although both show restricted light rare earth element enrichment (Ce/Yb_N = 1.79 and 1.29). Some of the EPR samples in this study were previously examined by Donnelly (2002) and Reynolds et al. (1992).

Within the clusters of samples two detailed subsets were analyzed. Firstly, six samples ("15.5°N group"; Fig. 1) come from closely spaced dredges collected in 1997 during an examination of a small magma lens around 15.5°N latitude (Donnelly, 2002). Three of the samples from this group (PANR1-D30A, -D30B, -D30C) are from a single wax core and range from relatively unevolved (MgO 6.55 wt.%) to highly evolved (MgO 1.75 wt.%). Four samples analyzed for halogen

contents exhibit a significant range in so-called excess chlorine (after Michael and Cornell, 1998) expressed as Cl/K values of 0.04–0.32 (le Roux et al., 2006). Chlorine and K are similarly incompatible during MORB melting and fractional crystallization, hence their ratio should remain constant during these processes. Elevated values indicate addition of chlorine from external sources.

Secondly there is a group of four samples ("9.5°N group"; Fig. 1) collected from locations at around 9.5°N latitude. All but one sample (ALV2759-005) was determined to have been erupted off-axis (Goldstein et al., 1994). The samples are similarly moderately evolved (MgO 6.35–7.22 wt.%), with a range of excess chlorine (Cl/K = 0.04–0.65; le Roux et al., 2006). There is a substantial difference in the sea floor between the two detail sample sites: the 9.5°N group comes from both deeper (by c. 500 m) and much faster spreading (by c. 20 mm/a) crust than the 15.5°N group.

2.2. Handling and analysis

We have chosen only glassy samples for analysis. With few exceptions samples have been handpicked under microscope from sub-millimeter chips so as to comprise only visibly unaltered glass (see Table 1). Samples have not been leached in acid solutions out of concern for inducing isotopic fractionation in the process. Samples have been rinsed with methanol and distilled H_2O at room temperature only.

Ion exchange separation of Li from samples and subsequent isotopic analysis use the methods established by Tomascak et al. (1999a), in which Li is eluted using a mixture of dilute nitric acid and methanol. Isotopic fractionation during laboratory ion exchange is assessed and circumvented by a combination of conservative elution volumes and mass spectrometric verification that elution volumes taken before and after the Li aliquot contain insignificant amounts of Li. Most material was prepared at the Lamont–Doherty Earth Observatory, but a small number of samples were prepared by identical techniques at the Department of Geology, University of Maryland. Measurements were by multiple collector sector ICPMS at the Carnegie Institution of Washington (VG Plasma 54–30) and at Maryland (Nu Plasma). In each case sample introduction used low-uptake desolvating nebulizers. In both laboratories the estimated external reproducibility of isotope measurements, based on multiple duplicate and replicate analyses, is $\pm 1.1\permil$ (2σ). A number of the same solutions analyzed at Carnegie were run later at Maryland, and no resolvable cross-instrumental bias was evident (Fig. 2). Given the high degree of inter-laboratory cross-instrumental agreement, the estimated uncertainty is likely a modest overestimate of the true reproducibility of the data presented here. We use the average isotope ratio for sample solutions analyzed with both instruments.

Lithium concentrations were determined by quadrupole ICPMS at Harvard University. The data reported in Table 2

represent averages of duplicate analyses of individual preparations. These analyses had a mean reproducibility better than 4.6% (2σ). Replicate analyses of standard reference materials JB-2 (8.1 ppm), BHVO-2 (4.7 ppm) and DNC-1 (5.3 ppm) yielded values consistent with modern recommendations (Govindaraju, 1989; Jeffcoate et al., 2004).

3. RESULTS AND DISCUSSION

3.1. Global Li data

The Li concentrations of the samples from this study overlap the range determined on a larger data set by Ryan and Langmuir (1987). The study of Ryan and Langmuir included a larger proportion of more primitive samples than this study (46% versus 13% samples with $\geqslant 8$ wt.% MgO), and so their mean Li concentration in MORB was slightly lower than that determined here (5.6 ppm versus 6.7 ppm, excluding samples with MgO < 6 wt.%). The Li concentration of average EPR basalts is systematically higher than samples from either the IR or MAR (7.2, 5.8 and 5.4 ppm, respectively, for samples with >6 wt.% MgO), consistent with previous data (Elliott et al., 2006; Ryan and Langmuir, 1987).

Although adding significantly to the overall data set for MORB, this study is consistent with earlier work in that there is restricted isotopic variability (Table 2; Fig. 3). The combined 30 samples define a small overall range in δ^7Li (+1.6 to +5.6; mean = +3.7). This overlaps the range found originally by Chan et al. (1992). The range for N-MORB (+2.5 to +4.7) is essentially identical to that for samples with higher K_2O/TiO_2. Basalt samples with $K_2O/TiO_2 > 0.4$ show a slightly higher mean δ^7Li (+4.0 versus +3.4 for N-MORB), although the difference is within analytical uncertainty. There is no analytically significant difference between the mean δ^7Li of samples from different ridge systems (MAR: +3.9; IR: +4.1; EPR: +3.5). Taken as a whole, δ^7Li in the global MORB data set does not appear to correlate with major (Figs. 4, 5A) or trace elements (Fig. 5B and C) or radiogenic isotopes (e.g., $^{87}Sr/^{86}Sr$; Fig. 5D). Limited $\delta^{18}O$ data from a group of the MAR samples also show no correlation with δ^7Li (Cooper et al., 2004).

3.2. Lithium in the individual ridge segments

Trace element enriched samples proximal to the Azores triple junction show no systematic Li isotope effect. Sample AII0127-2-046-011T3, from a group north of the Oceanographer fracture zone, has high K_2O/TiO_2 and records the heaviest isotopic signature of the entire data set ($\delta^7Li = +5.6$). Other samples from that area with similarly high K_2O/TiO_2 show no such heavy enrichment. On average there is a slight Li isotopic difference between samples from the deepest MAR regions (mean $\delta^7Li = +3.9$ for depths >2700 m) and those from the shallowest parts of the ridge (+4.7 for depths < 2300 m). Nevertheless, the mean values overlap within uncertainty.
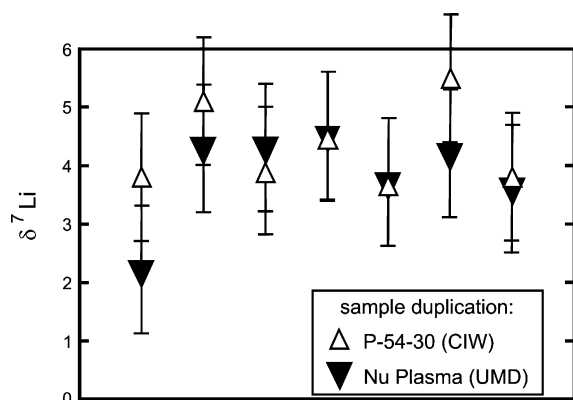

Fig. 2. Comparison of solution analyses by MC-ICPMS at the Carnegie Institution of Washington (P-54-30 instrument; white symbols) and the University of Maryland (Nu Plasma instrument; black symbols). Error bars are the experimentally determined uncertainty of $\pm 1.1\permil$ (2σ). Analyses of the same solutions with different instruments indicate that no analytically significant bias was introduced.

Table 2
Isotopic and elemental data for samples from this study

Locality sample number	δ⁷Li [*]	Li [**]	SiO₂	MgO	K₂O/TiO₂	⁸⁷Sr/⁸⁶Sr	(Ce/Yb)_N	Ba/Y
Mid-Atlantic Ridge								
AII0127-1-022-002	+4.1	5.40	51.9	6.03	0.474	0.703428	10.17	4.22
replicate	+3.8	5.32						
AII0127-1-018-002	+4.5	—	50.9	8.13	0.196	0.703239	1.49	3.32
AII0127-1-014-003	+3.8 [+2.2]	7.11	51.2	6.96	0.108	0.703302	0.71	1.27
AII0127-2-044GL	[+4.2]	4.83	48.2	7.72	0.850	0.704041	9.93	18.3
AII0127-2-045GL	[+2.4]	4.36	50.2	8.36	0.514	0.703678	—	8.12
AII0127-1-R018	+4.9	—	50.1	8.51	0.459	0.703515	—	—
AII0127-2-046-011T3	[+5.6]	5.87	49.9	7.75	0.570	0.703464	—	10.5
replicate		5.98						
ALV1016-001	[+3.2]	3.82	50.8	7.78	0.475	0.703411	2.69	6.26
AII0127-1-005	+3.9	4.37	49.3	9.03	0.075	0.702861	0.54	0.47
AII0127-1-001	+2.5	5.96	50.3	7.86	0.045	0.702745	0.59	0.24
replicate	[+2.5]							
OC180 17-3	+4.8	—	49.6	9.23	0.045	—	—	0.22
replicate	+4.2							
KNO0115-020	+5.1 [+4.3]	6.61	50.3	8.19	0.091	—	0.88	0.21
replicate		6.45						
Indian Ridge								
VEM0033-2-007-007	+3.9	5.74	49.9	9.11	0.129	0.703000	1.10	0.67
VEM0033-2-008-008	+4.6	5.57	51.0	7.97	0.288	0.703140	1.77	2.60
replicate		5.47						
VEM0033-2-010-003	+3.9	6.05	49.0	9.33	0.163	—	1.31	0.78
East Pacific Rise								
VE31-2	+3.9 [+4.3]	5.94	—	7.57	0.058	—	—	—
NHOCHEP-036-001	+4.5 [+4.5]	6.59	48.6	7.35	0.308	—	2.28	4.29
NHOCHEP-087-008	+4.7	6.70	50.3	7.60	0.053	—	—	0.41
NHOCHEP-082-008	+5.3	34.0	67.5	0.98	1.55	—	1.29	0.49
NHOCHEP-075-001	+3.8	7.59	49.9	5.98	0.246	—	2.59	3.39
15.5°N group:								
PANR1-D63-1	+3.1	7.63	51.2	6.84	0.159	—	—	—
PANR1-D22-1	+3.1	7.55	51.7	7.59	0.130	0.702850	1.07	1.32
PANR1-D29-5	+3.7 [+3.7]	8.08	51.3	6.68	0.209	0.702805	1.56	1.66
PANR1-D30A	[+2.0]	18.8	63.0	1.75	1.50	—	1.79	1.44
replicate		18.8						
PANR1-D30B	+3.8 [+3.6]	8.08	51.4	6.55	0.165	—	1.22	2.00
PANR1-D30C	+5.5 [+4.2]	13.2	53.2	3.89	0.288	0.703118	1.53	1.32
9.5°N group:								
ALV2759-005	[+1.6]	—	50.7	7.19	0.158	—	1.18	0.76
ALV2489-008	[+2.5]	—	50.6	6.35	0.201	—	1.47	1.87
ALV2489-009	[+2.5]	—	50.0	6.54	0.067	—	0.89	0.31
AII0125-24-R032-D	[+2.5]	—	49.5	7.22	0.071	—	0.83	0.29

Note. Major element concentrations in weight %; (Ce/Yb)_N = measured Ce/Yb normalized to chondritic.

— = data not available; replicate = separate digestion and measurement.

[*] Data in [] measured at UMD with Nu Plasma, others measured at DTM with P-54-30.

[**] Concentration (ppm) collected as part of this study; other elemental and Sr isotope data taken from the literature and from the PetDB online database (www.petdb.org).

All of the MAR samples from Chan et al. (1992) and Moriguti and Nakamura (1998) come from approximately 23°N, around the Kane fracture zone. These data ($n = 5$) span a range equivalent to that for all N-MORB. Our sample from near the Kane fracture zone (KNO0115-020) yielded a result within this range (+4.7).

The three samples examined from the IR have intermediate K₂O/TiO₂ (i.e., no N-MORB). Values of δ⁷Li range from +3.9 to +4.6. Sample collected west of the AAD have Li isotope compositions equivalent to samples collected within that zone. Lithium isotopes in these samples overlap the range determined for IR samples proximal to the Rodrigues Triple Junction (Nishio et al., 2007).

The EPR 9.5°N group samples have the lowest mean δ⁷Li of any of the sample groups examined (+2.2; Fig. 6). Samples from both the 15.5°N and 9.5°N groups with Cl/K ratios less than ~0.1 have lower average δ⁷Li than those with higher Cl/K, although the variations are within analyt-
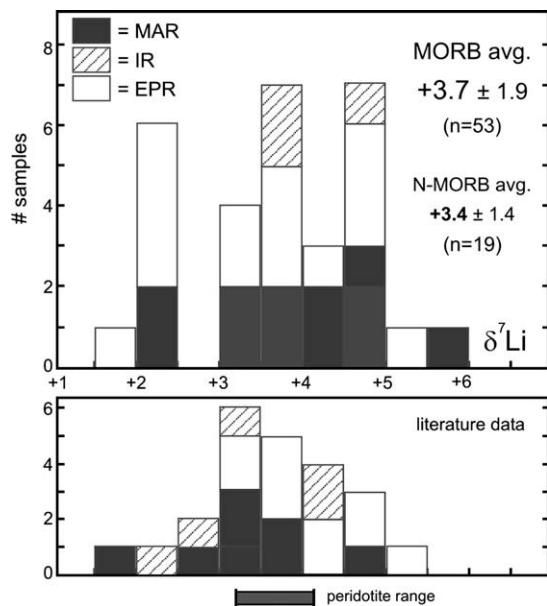
Fig. 3. Histogram of Li isotope compositions of the global MORB data set relative to ridge segment of origin (includes literature data: Chan et al., 1992; Elliott et al., 2006; Moriguti and Nakamura, 1998; Nishio et al., 2007). The average value of δ^7Li for the entire group of 46 samples is identical to that for the 30 samples analyzed in this study ($+3.7 \pm 2.1$ 2σ). This is indistinguishable from the average value for N-MORB (samples with $K_2O/TiO_2 < 0.09$). Included for reference is the range for pristine lithospheric mantle peridotites from Jeffcoate et al. (2007).

Fig. 4. Plots of (A) MgO, (B) SiO$_2$ (both in wt.%) versus δ^7Li for global samples (this study plus Elliott et al., 2006; Moriguti and Nakamura, 1998; Nishio et al., 2007). White symbols denote depleted samples with K_2O/TiO_2 (wt.%) < 0.09, black symbols are samples with $K_2O/TiO_2 > 0.4$, and split-color symbols are intermediate between these values. Symbol shapes denote ridge of origin, as in Fig. 1. Two non-basalt samples from the EPR with SiO$_2 > 55$ wt.% have been left off of B, for clarity (see text). Error illustrated is the 2σ for data in this study.

ical uncertainty. The presence of excess Cl was interpreted by le Roux et al. (2006) to reflect contamination effects of the shallow magma chamber.

3.3. Heterogeneity in global MORB

Taken together the world MORB data set (53 samples; this study plus literature data) gives a range in δ^7Li of +1.5 to +5.6. The global MORB data set for N-MORB ($K_2O/TiO_2 < 0.09$) gives a range in δ^7Li of +2.4 to +4.7 ($n = 19$). It is clear from these data that, as a whole, the MORB source is heterogeneous with respect to Li and no generally-applicable restricted δ^7Li signature in a given part of the ridge system can be assumed. For example, if Li in MORB reflects a mixture between a homogenous primitive mantle and a recycled component with a broadly homogeneous geochemical character, trends in δ^7Li versus Li (Fig. 5B) or other elemental concentrations should be produced. The absence of such correlations is consistent with MORB sources in which Li has been decoupled from other elemental/isotopic systems.

The Li isotope heterogeneity of MORB contrasts with the apparent homogeneity of the MORB source, as illustrated by peridotite data. Based on analysis of minerals and bulk samples of pristine continental lithospheric mantle xenoliths from two localities, Jeffcoate et al. (2007) recommended δ^7Li ~+3.5 for the undepleted upper mantle, consistent with values obtained in other studies (Brooker et al., 2004; Magna et al., 2006b; Seitz et al., 2004) for olivine and
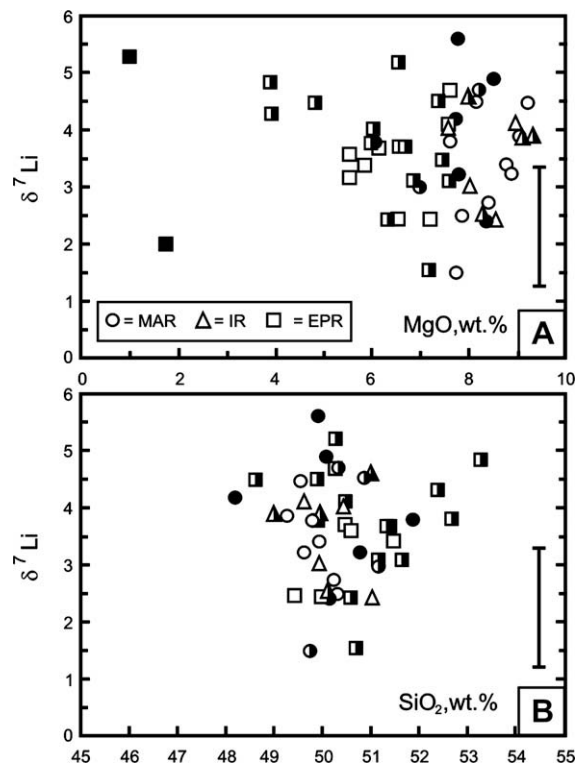
bulk rocks. From where does the greater isotopic variability in MORB (c. 5‰ versus c. 1‰ in peridotites) originate?

The absence of strong trends between Li isotopes and other geochemical indicators in the global data set suggests that MORB Li is not primarily influenced by a single, uniform process. However, isotopic variability outside analytical uncertainty is observed amongst these samples. Crystal fractionation in MORB systems can drive Li isotopic fractionation, but it is unlikely to lead to variations at the multiple per mil level (Chan and Frey, 2003; Jeffcoate et al., 2007; Tomascak et al., 1999b). The concentration data for samples with $K_2O/TiO_2 < 0.4$ are generally not consistent with variations resultant exclusively from crystal fractionation (Fig. 6). At least some of the elemental enrichments in the samples with $K_2O/TiO_2 > 0.4$ can be explained by crystal fractionation.

Alkali diffusion during melt-rock interaction/extraction in the MORB plumbing system can potentially explain Li isotope variations decoupled from other elemental systematics (Lundstrom et al., 2005). Diffusion of alkali elements from melt conduits or a shallow magma lens into surrounding mantle should result in selective loss of ^{6}Li from part of a MORB magma chamber, although the most peripheral
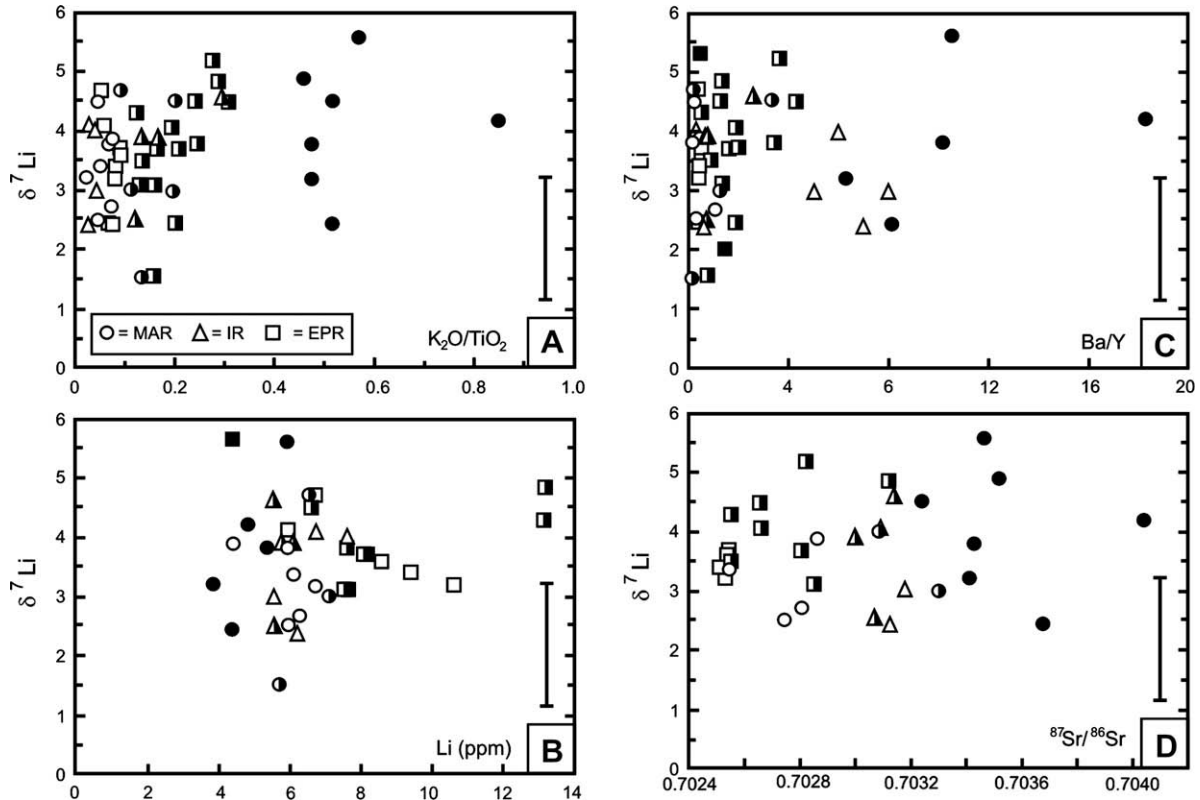
Fig. 5. Plots of (A) K_2O/TiO_2 (wt.%), (B) Li (ppm), (C) Ba/Y, (D) $^{87}Sr/^{86}Sr$ versus δ^7Li for the global data set (this study plus Elliott et al., 2006; Moriguti and Nakamura, 1998; Nishio et al., 2007). Symbols as in Fig. 4. Two non-basalt samples from the EPR with $K_2O/TiO_2 > 0.4$ have been left off of A and B for clarity (see text). Error illustrated is the 2σ for data in this study.
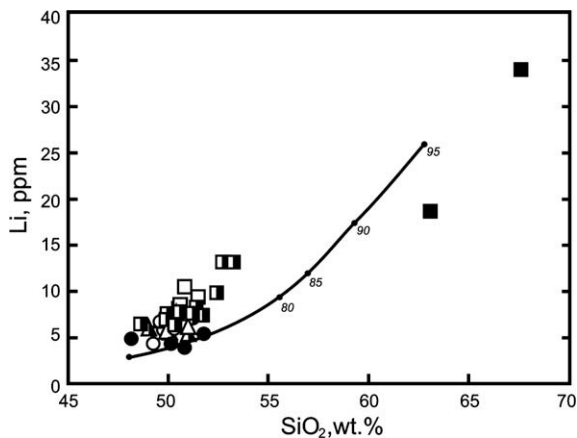

Fig. 6. Plot of SiO_2 versus Li concentration. Symbols as in Fig. 4. The curve represents model products of fractional crystallization of a basalt with 3.0 ppm Li and 49 wt.% SiO_2 ($D_{Li} = 0.28$, $D_{Si} = 0.91$; Dunn and Sen, 1994; Kennedy et al., 1993) with tic labels showing percent crystallized. The bulk of the data do not follow this trend, suggesting Li enrichment by means other than crystal fractionation. Only the enriched samples show particular consistency with crystal fractionation control of these elements.

samples under the right circumstances in MORB magma chambers. Lundstrom et al. (2005) indicated that evidence of diffusion processes might be muted in settings where the ratio of melt to rock is high (as in MOR). Given the likelihood that melts from various parts of an individual MORB plumbing system undergo significant homogenization, the likelihood of preserving much Li isotopic heterogeneity by this method is not great. Thus we conclude that diffusion is most likely to have a small pervasive influence on Li isotopes in MORB, not at the level needed to account for the observed range in the global data set. It appears more plausible that Li isotope variations in unaltered MORB samples must derive from mixing or assimilation processes involving isotopically distinct materials. We explore these hypotheses below.

3.4. Mixing of recycled components and shallow-level assimilation

It is clear that simple mixing on a global scale is inadequate to explain the lack of correlation between Li isotopes and other geochemical indicators. The scale of sampling, however, is likely to have some influence on the manifestation of such correlation. The very different geologic and tectonic settings of the samples of the global study may serve to mask true variations within individual magmatic systems of the ridge. In some regions where more closely spaced samples were examined, correlations begin to appear, but

melts could carry this light-enriched Li with them. If these melt parcels failed to homogenize subsequently, it would be possible to generate both isotopically heavier and lighter

not universally. In one of the two sets of samples examined from the EPR (the 15.5°N group), correlations exist between Li isotopes and several elemental concentrations, the strongest being K ($R^2 = 0.975$), Li ($R^2 = 0.931$) and Mg ($R^2 = 0.930$). Nonetheless in other locations where samples are relatively clustered (e.g., between 35.12°N and 35.33°N on the MAR) no such correlations are apparent.

Elliott et al. (2006) interpreted correlation between δ^7Li and radiogenic isotope and incompatible trace element concentrations for basalt glasses from two localities on the EPR to be most consistent with incorporation of recycled subduction-metasomatized upper mantle in the MORB source. Notably, the samples showed no Li isotopic variation outside the range determined in the current study (δ^7Li = +3.1 to +5.2). Correlated Li and Nd isotopes were used to argue against magma chamber contamination by seawater-altered components, as these should show little Nd isotope heterogeneity. The study of Elliott et al. (2006) implies that Li isotopes have a capacity to resolve small-scale heterogeneities in the MORB source which originate from recycling of subduction-processed material that persist in the upper mantle, as has been long considered on the basis of other geochemical indicators (e.g., Allègre et al., 1984; Eiler et al., 2000; Ito et al., 1987; Sun et al., 1979).

More localized phenomena could play a significant role in creating Li isotope heterogeneity unrelated to the bulk upper mantle. Both large-scale seawater circulation and shallow-level magma chamber incorporation of seawater-affected components (e.g., Danyushevsky et al., 2000; Michael and Schilling, 1989) could alter an originally homogeneous

MORB Li isotope composition without significantly affecting many other elemental and isotopic systematics. Low-temperature altered basalt, brines, and other materials that equilibrate with seawater have δ^7Li substantially higher than the MORB average (Chan and Edmond, 1988; Chan et al., 1992). Therefore, contamination of MORB magmas with these components would drive δ^7Li to higher values.

In Fig. 7 the Li isotope data from the EPR detail sample sets are compared to their differentiation-normalized Cl contents. Calculations were completed for the mixing of a variety of hypothetical components with a depleted mantle end member. Although Cl concentrations for some of these materials are either variable or not well characterized (see Table 3), the quantities chosen are meant to be broadly illustrative. The plot considers both components that would appear as the result of long-term recycling through the upper mantle (e.g., subduction-modified mantle, eclogite) and those that would be expected during shallow-level assimilation by an evolving magma chamber (e.g., altered oceanic crust, seawater, saline brine). The estimate for recycled subarc mantle is based on a metasomatized peridotite from Brooker et al. (2004). The altered basaltic crust estimate uses a relatively high Cl concentration relative to literature data (e.g., Jambon et al., 1995), so that the mixing curve thus generated represents maximum values of Cl/K. The brine estimate is a composite of the 15% NaCl solution modeled by Kent et al. (1999) and hydrothermal vent fluids examined by Chan et al. (1993). Owing to the high chlorinity of this end member, the model is rather insensitive to the estimates of Li and δ^7Li at low weight fractions of assimilation.
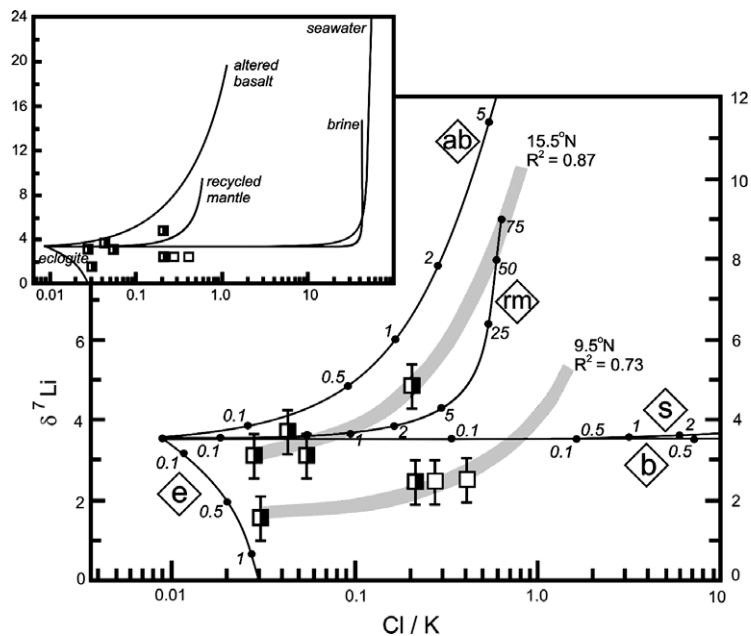

Fig. 7. Plot of Cl/K versus δ^7Li for the two detail sample sets from the EPR. Elemental data are from le Roux et al., 2006. Symbols are as in Fig. 4. Solid lines are model mixtures of mantle peridotite (low Cl/K and δ^7Li) with a variety of components: seawater (s), saline brine (b), altered ocean crust (ab), recycled subarc mantle (rm), and eclogite (e) (see text for discussion and references). Tic marks represent % weight fraction additions to the mantle end member. Shaded trends represent best-fit linear regressions of the four data in each group. The inset expands the scales for broader reference.

Table 3
Parameters used in mixing models

Element/isotope	Mantle source	Seawater	Brine	Altered ocean crust basalt	Recycled mantle	Eclogite
Li (ppm)	1.6 (1)	0.18 (4)	0.15 (7)	27 (9)	4.1 (11)	40 (12)
Cl (ppm)	0.5 (2)	19350 (5)	99000 (8)	1000 (10)	579 (11)	200 (13)
K (ppm)	60 (2)	400 (5)	2075 (8)	830 (10)	946 (11)	3569 (12)
$\delta\,^7Li$	+3.5 (3)	+31 (6)	+15 (7)	+20 (9)	+9.6 (11)	−11 (12)

Note. Number in parentheses is reference for data, (1) Ottolini et al., 2004; (2) Salters and Stracke, 2004; (3) Jeffcoate et al., 2007; (4) Chan and Edmond, 1988; (5) Broecker and Peng, 1982; (6) Millot et al., 2004; (7) Chan et al., 1993; (8) Kent et al., 1999; (9) Chan et al., 1992; (10) Jambon et al., 1995; (11)Brooker et al., 2004; (12) Zack et al., 2003; (13) Philippot et al., 1998; see text for details.

Samples from the 15.5°N group show correlation between δ^7Li and Cl/K ($R^2 = 0.875$) consistent with the incorporation of a heavy-Li-enriched component that has elevated Cl/K, although the spread in Li isotopes for the four samples is within analytical uncertainty. Also, the trend in the 15.5°N data is, like the trend in δ^7Li versus ε_{Nd} for EPR MORB samples from Elliott et al. (2006), strongly controlled by one relatively isotopically heavy sample. The data fall most closely to the mixing curve for a recycled subduction-metasomatized mantle component, with the isotopically heaviest sample reflecting <5% (weight) assimilation of this end member. Inasmuch as the mixing curve for altered oceanic crust is intended to reflect maximum Cl/K, this component appears to provide a poorer analog for the trend of the data.

The modest correlation between Li isotopes and Cl/K amongst 9.5°N group samples is most consistent with contamination by a seawater-related component, although the spread in δ^7Li is well within analytical uncertainty. This conclusion is consistent with the results of le Roux et al. (2006), based on water, halogen and other elemental constraints. This model does not permit differentiation between incorporation of seawater versus an isotopically lighter brine constituent; both would require less than 0.5% assimilation of these components to have the effect on Cl/K. The 9.5°N group samples show very little spread in MgO content, and it is not correlated with δ^7Li or Cl/K. Consequently, if the δ^7Li-Cl/K trend is genuinely the record of small extents of magma chamber contamination, the added component was more likely saline brine than bulk Mg-rich altered crust, consistent with previous work (Michael and Schilling, 1989).

If the trends from the EPR data in Fig. 7 are extrapolated back to presumed "uncontaminated" mantle Cl/K, they do not appear to converge on a single value like average N-MORB. Contrarily, le Roux et al. (2006) found continuity between the estimated uncontaminated elemental compositions of mantle end-members from sample groups around 9–10°N and 12–14°N on the EPR. The 15.5°N group samples define a source value of $\delta^7Li \sim +3.0$, broadly consistent with N-MORB and with the sources inferred from the data of Elliott et al. (2006). The 9.5°N group suggests a source with $\delta^7Li \sim +1.7$. A mantle source with δ^7Li lower than the peridotite value of +3.5 is consistent with the extrapolations of arc data in two tectonically distinct settings (Izu: Moriguti and Nakamura, 1998; southern Cascades: Magna et al., 2006a). Hence, despite the evidence for a homogeneous MORB source mantle with $\delta^7Li \sim +3.5$, Li isotopes in both MORB and arc lavas point to regional MORB source heterogeneity not yet discovered in unmetasomatized peridotites. Upper mantle domains with Li isotopically lighter than pristine peridotites can be explained by mixing small fractions of recycled eclogite (<1%; Fig. 7).

Since these data were collected, methods have been reported that extend Li isotope measurement to sub-permil 2-sigma precisions ($\pm \leqslant 0.5‰$, Magna et al., 2004; ±0.3‰, Jeffcoate et al., 2004; ± 0.24‰, Millot et al., 2004). The expanded data set makes it clear that an improved level of precision will be necessary in order to fully interpret the variations of Li isotopes in MORB. Furthermore, studies that systematically analyze groups of samples from individual ridge segments are needed to make significant progress toward understanding Li isotopes in MORB.

4. SUMMARY

When a globally dispersed, chemically diverse data set is considered, the MORB reservoir reveals broad heterogeneity with respect to Li isotopes, with an overall mean δ^7Li of +3.7 (range = +1.5 to +5.6; $n = 53$ for this study plus published data), indistinguishable from the mean for the samples that show the highest degrees of incompatible trace element depletion (N-MORB: mean = +3.4; range = +2.4 to +4.7; $n = 19$). Basalts with $K_2O/TiO_2 > 0.4$ show some higher values of δ^7Li (range = +2.4 to +5.6; $n = 7$), but substantially overlap the N-MORB range. To the limit of the data we have collected and the analytical precision, there appears to be no large-scale provinciality in Li isotopes in the major segments of the global ridge system, nor observable effects imposed by variations of bathymetry or spreading rate. The lack of systematic co-variation between Li isotopes and elemental or radiogenic isotopic parameters indicates that a globally well-mixed and isotopically homogeneous MORB reservoir should not be assumed. Rather we argue that Li in the MORB source retains small scale isotopic heterogeneity. Some heterogeneities may reflect the incorporation of recycled mantle components from large-scale flow through the upper mantle. In other cases the data more closely follow trends established by assimilation within individual magma plumbing systems of seawater-derived components.

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