LETTERS

Lithium isotope evidence for subduction-enriched mantle in the source of mid-ocean-ridge basalts

Tim Elliott[1], Alex Thomas[1,2], Alistair Jeffcoate[1]† & Yaoling Niu[3]

'Recycled' crustal materials, returned from the Earth's surface to the mantle by subduction, have long been invoked to explain compositional heterogeneity in the upper mantle[1]. Yet increasingly, problems have been noted with this model[2,3]. The debate can be definitively addressed using stable isotope ratios, which should only significantly vary in primitive, mantle-derived materials as a consequence of recycling. Here we present data showing a notable range in lithium isotope ratios in basalts from the East Pacific Rise, which correlate with traditional indices of mantle heterogeneity (for example, $^{143}Nd/^{144}Nd$ ratios). Such co-variations of stable and radiogenic isotopes in melts from a normal ridge segment provide critical evidence for the importance of recycled material in generating chemical heterogeneity in the upper mantle. Contrary to many models, however, the elevated lithium isotope ratios of the 'enriched' East Pacific Rise lavas imply that subducted ocean crust is not the agent of enrichment. Instead, we suggest that fluid-modified mantle, which is enriched during residency in a subduction zone, is mixed back into the upper mantle to cause compositional variability.

The Li isotope system can provide a novel perspective on the role of recycled material in the mantle, but is yet to be fully exploited in studying geodynamic problems[4]. Subduction delivers altered oceanic crust and underlying serpentinized peridotite with heavy Li (that is, elevated $^{7}Li/^{6}Li$ or high $\delta^{7}Li$) to the mantle[5,6]. Heavy $\delta^{7}Li$ in mantle-derived melts should therefore be a diagnostic tracer of recycled material. This simple scenario is made more interesting by processes that occur during subduction: altered oceanic crust loses its isotopically heavy Li to the overlying mantle in the subduction zone[7,8] and ultimately becomes isotopically light as a consequence of its dehydration[9,10]. Addition of recycled material can hence lower or raise the Li isotope ratio of the mantle, depending on whether the oceanic crust itself or subduction-modified mantle is the main agent of 'enrichment' (Fig. 1). Here we present the first Li isotope data on mid-ocean-ridge basalts (MORB) with suitable precision to identify possible recycled contributions.

We have analysed ten well-characterized samples[11,12] from two locations (~10° 30′ N and ~11° 20′ N) on a morphologically typical ridge segment of the East Pacific Rise (EPR). The location at ~11° 20′ N is marked by an anomalously large number of 'enriched' MORB[11]. Similarly enriched samples from 11° 30′ N and 12° 50′ N EPR were argued to be derived from mantle-containing recycled oceanic crust[13]. Samples from ~10° 30′ N are more normal, 'depleted' MORB. All samples provided sufficient material to allow rigorous hand-picking of pristine glass. Li isotopes were measured on 2–10 mg samples of glass, processed by two-stage separation chemistry and analysed by multi-collector, inductively coupled plasma mass spectrometry[14]. Each separated sample was analysed at least twice and showed a reproducibility that was typically better than

±0.15‰ (2 standard deviations, 2 s.d.; Table 1 and Supplementary Information). Full repeat measurements of two samples for which there was sufficient glass and triplicate analyses of international standard BHVO-2 (Table 1 and Supplementary Information) reproduced results that were in-line with our long-term estimate of repeatability, ±0.3‰ (2 s.d.)[14]. Our analytical procedure allowed small variations in Li isotope ratios to be detected: these variations
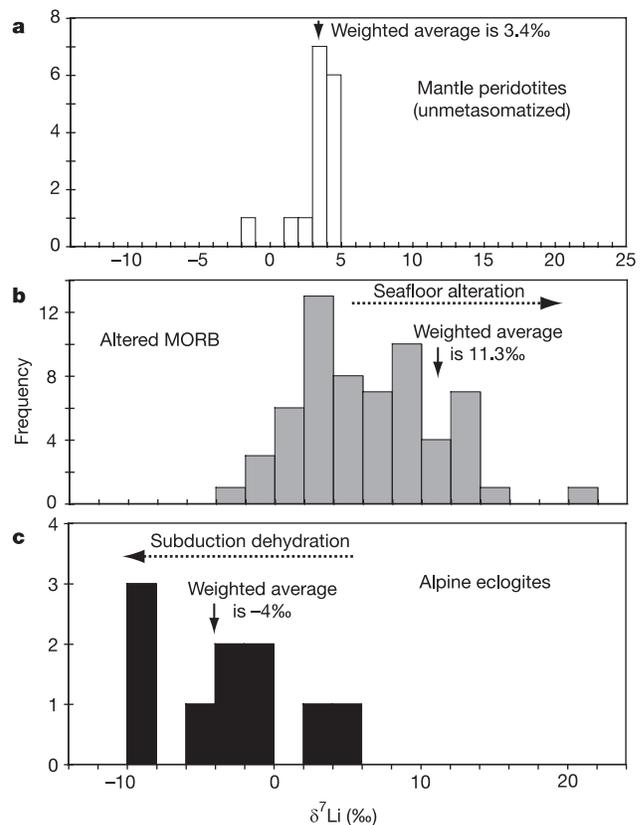
Figure 1 | Li isotopic compositions of the mantle and important recycled components. Histograms of $\delta^{7}Li$ for: **a**, modally unmetasomatized peridotites[17–19], taken to represent the most pristine shallow mantle (peridotite compositions are reconstituted from modal abundances and analyses of their constituent minerals for refs 17 and 18, and from bulk analyses for ref. 19); **b**, MORB altered by low-temperature interaction with sea water[5,20]; and **c**, Alpine eclogites[9,19]—tectonically exhumed fragments of mafic material interpreted to represent dehydrated, deep subducted oceanic crust. The average values reported in the figures were calculated by weighting individual isotopic analyses according to their Li concentrations.

[1]Bristol Isotope Group, Department of Earth Sciences, Wills Memorial Building, Queen's Road, University of Bristol, Bristol BS8 1RJ, UK. [2]Department of Earth Sciences, South Parks Road, Oxford University, Oxford OX1 3PR, UK. [3]Department of Earth Sciences, Durham University, Durham DH1 3LE, UK. †Present address: Rio Tinto Iron Ore Atlantic, PO Box 695, 8th Floor, Castlemead, Lower Castle Street, Bristol BS99 1FS, UK.

would have been unresolved in previous Li isotope studies of MORB[5,15,16], which had uncertainties of ±0.7–1.5‰ (2 s.d.; Fig. 2a). We report our Li isotope analyses in Table 1 as δ^7Li, that is, the parts per thousand variation of ^{7}Li/^{6}Li relative to the standard NIST SRM 8545 (L-SVEC).

The δ^7Li of our samples ranges from 3.1 to 5.2‰ (Fig. 2) and so we are able to document Li isotope heterogeneity well beyond analytical uncertainty. The normal, depleted MORB samples have the lowest δ^7Li, with values similar to the average of unmetasomatized mantle peridotites[17–19] (Fig. 1a). Notably, our MORB Li isotope ratios show good correlations with a range of conventional elemental and isotopic indices of enrichment (Fig. 2). Heavier Li isotope ratios are associated with higher incompatible element concentrations (Fig. 2a), elevated ratios of highly incompatible to moderately

incompatible elements (Fig. 2b), distinctive highly incompatible element ratios (for example, Fig. 2c), more radiogenic ^{87}Sr/^{86}Sr (Fig. 2d) and less radiogenic ^{143}Nd/^{144}Nd (Fig. 2e).

Variations in the stable isotope ratios of mantle-derived rocks are an unequivocal signature of recycled material in their sources, provided they have not been modified by processes *en route* to the surface. It is thus necessary to assess processes that may have perturbed the primary δ^7Li of the magmas. Low-temperature alteration of the upper oceanic crust generates secondary minerals with high Li concentrations and heavy δ^7Li (refs 5, 20). Assimilation of this material could increase Li isotope ratios but should little affect absolute or relative abundances of elements unsusceptible to alteration and so cannot account for the trends observed in Figs 2b, c, e. Moreover, there is no correlation of 1/Li with δ^7Li in our data set (not shown) and the full range of our observed Li isotope variation is defined by two samples (PH 108-1 and PH 54-3) that are comparably differentiated (for example, 6.5 versus 7.0 wt% MgO) and have similar Li concentrations (6.8 and 6.9 µg g^{-1}). Thus, heavy Li isotope ratios cannot represent the effects of preferential assimilation of Li-rich material at shallow levels. Mixing of more primitive magmas with anatectic melts of the magma chamber roof[21] can potentially generate secondary variations in both abundances and ratios of 'fluid-immobile' elements and even ^{87}Sr/^{86}Sr, but cannot account for changes in ^{143}Nd/^{144}Nd. Therefore, interaction of mantle-derived melts with the crust seems unable to account for the geochemical variations we observe in the northern EPR.

It is also important to consider possible high-temperature fractionation of Li. Equilibrium isotopic fractionation of Li between melt and typical mantle peridotite is minor (<0.5‰)[18]. Likewise, differentiation of basaltic melts in Hawaii has been shown to cause no
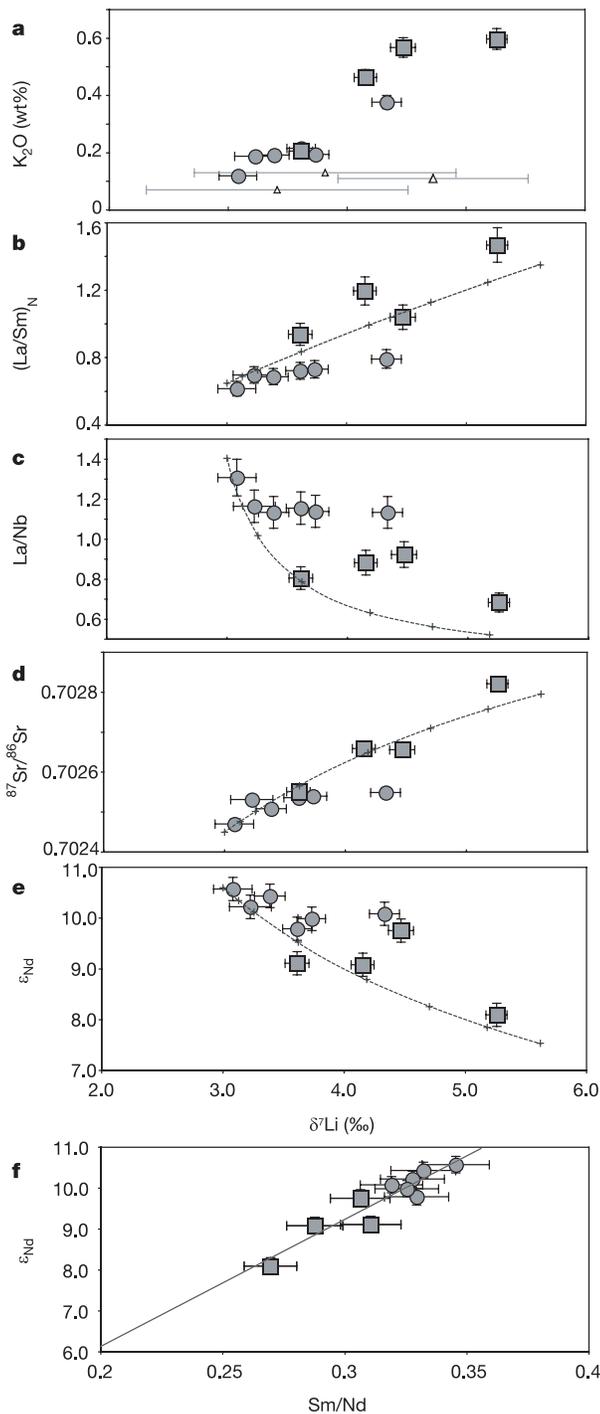
Figure 2 | Variations of δ^7Li with other geochemical parameters in northern EPR MORB. a–e, δ^7Li is plotted against: **a,** K$_2$O (wt%), together with previously published MORB[5] analysed for both Li isotopes and K$_2$O (open triangles); **b,** chondrite normalized[29] La/Sm; **c,** La/Nb (weight ratio); **d,** ^{87}Sr/^{86}Sr; and **e,** ε_{Nd} (parts per 10^4 relative deviation of ^{143}Nd/^{144}Nd from the present chondrite reference value of 0.512638) **f,** Sm/Nd (weight ratio) is plotted against ε_{Nd}, together with a best fit line, which can be used to calculate an apparent age of enrichment (400 Myr ago). The 10° 30′ N samples are plotted as filled circles and 11° 20′ N samples are shown as filled squares. Apart from Li isotope measurements, the data are from refs 11, 12. The dashed lines in **b–e** are mixing curves between a hypothetical depleted upper mantle source with δ^7Li = 3‰, [Li] = 1.5 µg g^{-1}, [Nb] = 0.29 µg g^{-1}, [La] = 0.4 µg g^{-1}, [Nd] = 1.4 µg g^{-1}, [Sm] = 0.55 µg g^{-1}, [Sr] = 14 µg g^{-1} and the amphibole peridotite BZ72 (ref. 8), proposed to represent subduction-modified mantle. The composition of the depleted mantle is modelled by assuming that the most depleted sample of this study (PH 54-3) is the product of 10% mantle melting. Crosses indicate 0, 1, 2, 5, 10, 15, 20 and 25% (by weight) additions of BZ72 to the depleted mantle composition. Because there are no radiogenic isotope data reported for BZ72, we assume reasonable values of ^{87}Sr/^{86}Sr = 0.703 and ε_{Nd} = 5.9. The ^{87}Sr/^{86}Sr comes from an analysis of clinopyroxene separates from a similar, pargasite-bearing, Zarbagad peridotite—W36 (ref. 30). Given the low Rb/Sr of BZ72 (0.017) it is appropriate to use the ^{87}Sr/^{86}Sr value of a low Rb/Sr phase such as clinopyroxene. We inferred the Nd isotope value of the enriched endmember using the well-defined relationship in **f** and the measured Sm/Nd of BZ72 (0.194). Hence, there is some circularity in the fit of the mixing line in **e**, but since the other parameters used in its calculation are independent, the shape of the array still has some significance. The mixing trends shown in **b–e** serve to illustrate the general effects of addition of a single example of subduction-modified mantle to a normal MORB source, but were not necessarily expected closely to mimic the trends here. We did not model K$_2$O contents, which depend much more strongly than isotope and incompatible element ratios on assumptions about melting and fractionation, but note that BZ72 is a K$_2$O-rich peridotite (0.11wt%). Error bars show 2 s.d. of repeat sample measurements (a conservative reproducibility of 6% for K$_2$O abundances was used, otherwise errors are documented in Table 1 and ref. 11).

Table 1 | δ⁷Li measurements on EPR glasses

Sample	Latitude (°N)	Longitude (°W)	Depth (m)	MgO (wt%)	K₂O (wt%)	Li (µg g⁻¹)	δ⁷Li (‰)	Error 2 s.d.	n
PH78-2	10.43	103.86	3058	3.9	0.38	13.1	4.3	0.1	4
PH77-6	10.43	103.85	3051	5.8	0.19	9.4	3.4	0.1	2
PH65-1	10.45	103.64	2996	5.5	0.19	10.6	3.2	0.2	4
PH64-2	10.46	103.63	3008	5.5	0.22	8.6	3.6	0.1	3
PH62-1	10.48	103.63	2812	6.1	0.19	8.2	3.7	0.1	4
PH54-3	10.50	103.51	3069	7.0	0.12	6.9	3.1	0.2	4
PH108-1	11.34	103.79	2724	6.5	0.60	6.8	5.2	0.1	4
PHGC-60	11.35	103.77	2545	6.0	0.46	7.9	4.2	0.1	4
Repeat							3.9	0.1	2
PH103-2	11.37	103.78	2570	4.8	0.57	9.9	4.5	0.1	3
PH94-1	11.37	103.71	2863	7.4	0.21	6.3	3.6	0.1	4
Repeat							3.4	0.1	2
BHVO-2							4.8	0.3	4
Repeat							4.7	*0.1*	1
Repeat							4.7	0.1	3

Errors reported as 2 s.d. of repeat measurements of the sample solution (n is number of repeat measurements). All individual measurements are documented in Supplementary Information. One BHVO-2 replicate was run only once and so the standard error of the run rather than the standard deviation of repeats is reported (in italics). Analyses of full repeat dissolutions (Repeat) of samples are reported on separate lines. Additional information on the samples was obtained from refs 11, 12. $\delta^{7}Li = [(^{7}Li/^{6}Li)_{sample}/(^{7}Li/^{6}Li)_{NIST\,SRM8545} - 1] \times 1000$.

systematic change in $\delta^{7}Li$[22]. Finally, it has been argued that a diffusive mechanism of high-temperature Li isotopic fractionation could increase the $\delta^{7}Li$ of erupted magmas as a result of melt–peridotite interaction[23]. Whether such a process typically operates beneath mid-ocean ridges remains unclear. Moreover, any variations of $\delta^{7}Li$ thus produced are anticipated to be correlated with Li abundances, which is not the case.

Hence, we are confident that the heavy Li isotope signatures of the enriched MORB are a consequence of recycled material in their sources. This is a highly significant finding in itself but the heavy Li isotope signatures of enriched MORB provide additional constraints on the origin of the recycled component. Because dehydrated residues of deep, subducted oceanic crust are isotopically light[9,19], recycled oceanic crust itself cannot account for the heavy Li isotope characteristics of the enriched MORB (Fig. 2). This is contrary to many popular notions of recycling (for example, refs 1, 24).

The heavy Li that is thought to be lost from the subducting oceanic crust[9,10] is not evident in the Li isotope signatures of subduction zone volcanics[7] and so it is thought to be transferred into the mantle through which slab-derived fluids pass, by isotopic reequilibration[7]. An appealing candidate for the heavy $\delta^{7}Li$, enriched material beneath the EPR is thus mantle that once overlaid the dehydrating slab[4]. A similar model has recently been invoked to account for other chemical signatures of enriched MORB[25,26] and is consistent with the generally elevated $\delta^{18}O$ of such basalts in a high precision, global survey[27]. Oxygen isotopes, however, do not clearly distinguish between subduction-modified mantle and subducted oceanic crust and it was previously argued that a contribution of recycled crust was responsible for the heavy $\delta^{18}O$ values measured in enriched MORB[27].

The complexity and range of the subduction processes make it difficult to model in detail the composition of subduction-modified mantle. As an illustrative calculation, however, we have used the composition of an amphibole peridotite (BZ 72) which has been analysed for Li isotopes and has been argued[8] to record subduction zone enrichment. Not unexpectedly, the mixing curves of depleted mantle with this single amphibole peridotite (Fig. 2b–e) do not perfectly mimic the arrays of the EPR samples, but the general trends of Li isotope ratios with key tracers are well reproduced. Notably, mixing of the amphibole peridotite with depleted mantle can account for the decreasing La/Nb with increasing $\delta^{7}Li$ in our samples (Fig. 2c). It might seem counter-intuitive that our enriched component should have low La/Nb, as arc lavas typically have high La/Nb and, by inference, so will slab-derived fluids or melts that invade the mantle at subduction zones. Yet solid–fluid partitioning, in addition to the fluid composition itself, will influence the nature of sub-arc mantle enrichment. In particular, the growth of hydrous mineral phases might change the behaviour of elements normally considered to be highly incompatible. In our modelled scenario, the presence of amphibole in BZ72 provides a significant host for Nb. Variable conditions of mineral stability between and within subduction zones, as well as different fluid compositions, can potentially lead to a variety of elemental enrichment patterns in subduction-modified mantle.

Subducting, mafic oceanic crust has radiogenic $^{87}Sr/^{86}Sr$ as a result of seafloor alteration and so the elevated $^{87}Sr/^{86}Sr$ of the enriched component (Fig. 2d) is again consistent with the isotopic exchange of slab-derived fluids with the overlying mantle. The Pb isotopes of our EPR samples[11,12] show no systematic variations and are unremarkable for MORB (not shown), suggesting there is no sedimentary component in the subduction-enriched mantle identified here. Therefore, the unradiogenic Nd isotope signature of the enriched component is not an instantaneous product of subduction enrichment, but a consequence of subsequent evolution. At face value, the correlation of Sm/Nd with ε_{Nd} for the EPR basalts (Fig. 2f) could imply that an appropriate endmember was created by enrichment of a portion of depleted mantle at ~400 Myr ago. Other researchers[25] have noted similar apparent timescales between enrichment and magmatic sampling in Atlantic MORB, which they argued to represent residence times of enriched material in a continuously mixing upper mantle rather than discrete events.

From a physical perspective it is appealing that subduction-modified mantle is responsible for heterogeneities in the upper mantle. Subduction-modified mantle, initially chilled and viscously coupled to the down-going plate will warm, spall away and remix with ambient upper mantle. In contrast, the oceanic crust itself probably remains denser than the surrounding mantle and can potentially continue to sink even after it has become thermally equilibrated[28]. Subduction-modified mantle is thus naturally mixed back into the upper mantle more efficiently than the subducted crust. The fate of the oceanic crust itself thus remains enigmatic[3].

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