# The control of lithium budgets in island arcs

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## Abstract

Measurements of the Li isotopic compositions of lavas from magmatic arcs worldwide suggest common processes at work that lead to the retention of isotopically heavy Li in the mantle. Samples from this study derive from the Kurile arc, eastern Russia, the Sunda arc, Indonesia, and a segment of the Aleutian arc, western Alaska. The overall range in $\delta^7$Li is very restricted (+2.1 to +5.1 ± 1.1, 2$\sigma$) for 34 of 36 samples. These values overlap the values of unaltered normal MORB glasses. The two samples with isotopic compositions that fall outside this range in $\delta^7$Li have B/Be < 13, and hence do not bear classical 'slab' trace element signatures. Considering the high $\delta^7$Li in altered ocean crust, marine and terrigenous sediments, and forearc fluids, aqueous components lost by subducting slabs are expected to have similarly heavy enriched Li isotope signatures. If Li behaves similarly to a fluid-mobile element such as B, $\delta^7$Li should correlate strongly with, for example, B/Be. As such, samples with high B/Be should show elevated $\delta^7$Li. The sample set we have examined does not show such correlations and is interpreted to reflect a globally significant process. Although Li is a fluid-mobile element, its partitioning into Mg-silicates may cause it to be effectively removed during equilibration with subarc mantle peridotite. Elements with stronger fluid/mantle partitioning behavior, such as B, are not so affected. The convergence of Li isotope ratios on MORB-like values is interpreted to result from the sequestration of slab-derived Li in the subarc mantle before it reaches the zone of melting. The results indicate conditions appropriate for mantle 'buffering' of slab-derived Li are widespread in magmatic arcs. Alternately, some proportion of Li could be retained on the slab in high Li/B minerals. Either way, this indicates that regions of the upper mantle with $\delta^7$Li > MORB may be common, as a direct consequence of the subduction process. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The fundamental importance of light stable isotope systems such as Li and B in studies of magmatic arcs lies in the strong isotopic contrast between materials of broadly mantle prov-

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enance and those with near-surface histories. The strong crust–mantle isotopic fractionation of Li should lend itself to tracing the fate of subducted materials in the mantle and better quantifying their budgets. This relies, to an extent, on a finite mobility of Li during the process of subduction [1]: if Li is not transferred from subducting slab to mantle source region of arc magmas, an isotopic signal in arc magmas will not be present.

Because of the limited extant data, the Li isotopic compositions of mantle and slab components relevant to arc magmatism are not yet constrained systematically. However, the rapidly accumulating data support some general constraints on the character of these materials. Normal depleted MORB (mid-ocean ridge basalts with $K_2O/TiO_2 < 0.4$) are characterized by a narrow range in $\delta^7Li$ (+1.5 to +5.1) [2–4]. Slab-derived fluids are apparently enriched in heavy Li (i.e., $\delta^7Li > $ MORB) [5–7]. Several indirect constraints support this assertion.

Based on our current understanding, the Li isotopic compositions of the majority of materials that characterize the upper kilometer of subducting slabs (sediments and low-temperature altered ocean crust) overlap broadly and are high ($\delta^7Li > +5$), although there has been no detailed examination of the individual components of marine sediments, and there is some uncertainty about the effect of diagenesis on Li isotopes in some sediments [3]. Few data currently constrain the isotopic constitution of the lower part of the oceanic crust. Some hydrothermally altered basalts, serpentines from altered peridotites, and eclogites are isotopically lighter than MORB ($\delta^7Li \sim -15$ to $-1.5$) [2,3,8,9]. If such materials avoided low-temperature reaction with seawater, this could form a reservoir of isotopically light Li in the slab, although more thorough study is clearly needed. Other than this, there is little to support any abundance of material isotopically lighter than MORB in subducting slabs.

We have examined samples from three geologically and geochemically diverse magmatic arcs in an effort to understand more thoroughly the budget of Li during subduction. In each case, the arcs we have analyzed show elemental evidence to suggest prominent inputs of material deriving from the subducted slab. One reason for interest in a more comprehensive study of the behavior of Li in arcs is that the three published studies of Li isotopes in magmatic arcs to date (Izu [3]; Panama [10]; Central America [11]) reach different conclusions on the behavior of Li in this environment. In Izu, Li isotope composition correlates with fluid-sensitive element abundances, suggesting that Li is transported in fluids from the subducting slab to the arc magma sources in a manner essentially identical to B. Similar relations appear to hold for Nicaragua, although samples cover a much more restricted range in isotopic composition. In Panama the elemental systematics of Li and B are decoupled, such that older lavas with a strong slab B signature (high B/Be) carry no slab Li isotope signature. Young lavas with isotopically heavy (slab-like) Li signatures have very low, mantle-like B/Be. The decoupling was interpreted to reflect Li removal from slab fluids during fluid–peridotite interaction during early arc processes, followed by Li release from metasomatized peridotite in the more thermally mature arc. This study investigates whether the processes interpreted in the Panama subarc mantle are commonplace in the general process of subduction or if the Izu model is more globally applicable.

## 2. Geological background and samples

The samples from this study come from three globally dispersed and tectonically diverse oceanic arcs. We endeavored to analyze samples for which abundant supporting geochemical data are available. Each of the arcs studied is situated primarily on ocean crust, thus diminishing the potential for complications introduced by crustal assimilation. In any case, previous studies on these arcs do not indicate a significant influence from crustal interaction on the compositions of the lavas. Significant differences exist between the nature of sediment entering the subduction zones, the age of subducting crust, and, within each arc, the chemical composition of the lavas themselves. One similarity among these arcs is that some proportion

of the samples from each shows robust indications of chemical input of slab-derived material.

## 2.1. Kurile arc

The oceanic crust subducting beneath the Kurile arc is ∼120 Myr. Based on estimates from ODP cores, Plank and Langmuir [12] described the incoming sediment column as being dominated by siliceous ooze, with secondary chert and minor clay.

We have analyzed Quaternary Kurile arc samples used by Ishikawa and Tera [13] for B isotopes. Many of the same samples have been the subject of detailed trace element studies [14,15]. The samples contain 48.0–64.7 wt% $SiO_2$, 1.93–5.24 wt% MgO, and 0.63–1.95 wt% $K_2O$ [13–15]. Samples from this arc show strong correlation between $\delta^{11}B$ and indicators of slab fluid enrichment, such as B/Be and B/Nb, which also correlate negatively with depth to the subducting slab.

A set of five samples that traverse the arc across strike near Onekotan island have been analyzed. Ryan et al. [14] argued that this approach is the most likely to illustrate the distribution and budgets of slab components in magmatic arcs.

## 2.2. Sunda arc

Ocean crust subducting beneath the western and east-central parts of the Sunda arc is ∼80 to ∼130 Myr old. Estimated average sediment supply to the arc ranges from bimodal siliceous ooze and clays with minor turbidites beneath the western part of the arc to strongly clay-dominated material with secondary carbonate and minor siliceous ooze beneath to the east [12].

Both elemental and radiogenic isotopes indicate that the Sunda subarc mantle is heterogeneous along the length of the arc, as well as on the scale of a single volcanic center [16,17]. The samples come from three volcanoes on the island of Java and three volcanoes on and around the island of Flores, and are the same samples studied by Edwards et al. [18]. They span a range in bulk composition from tholeiites to high-K alkali basalts, with 43.9 to 63.4 wt% $SiO_2$, 1.80 to 18.1 wt% MgO, and 0.33 to 5.76 wt% $K_2O$ [17,18]. Unre-

lated to changes in bulk composition are large variations in trace elements, such as B/Be, taken to indicate variable slab inputs.

## 2.3. Aleutian arc

Ocean crust subducting beneath the central Aleutian arc in western Alaska is ∼25 Myr old [19]. Estimated sediment composition being delivered to the central Aleutian arc is dominated by siliceous ooze, with subordinate turbiditic material and minor clay [12].

Quaternary samples from the Aleutian arc that we have analyzed come from three separate volcanic centers: Okmok, Recheshnoi and Bogoslof. The former two volcanoes are near the volcanic front on the island of Umnak, whereas Bogoslof sits approximately 60 km behind the front. The Bogoslof sample, from the 1927 eruption, is a hornblende basalt with 5.40 wt% MgO [20]. The Umnak samples have 50.1–57.8 wt% $SiO_2$, 3.98–10.1 wt% MgO, and 0.86–1.33 wt% $K_2O$ [21], and show significant slab trace element signatures (e.g., Ce/Pb < 4.5) [22]. The samples were chosen to reflect various end member compositions, as defined on the basis of radiogenic isotopes and trace element contents by Class et al. [23]. Basal Recheshnoi sample LUM-21 is inferred to be derived from sources with a minor sediment melt influence and essentially no sediment fluid. Normal Recheshnoi sample LUM-17 bears the signature of a significant sediment melt source component as well as a substantial input from sediment fluid. The sample from Okmok, Qaf-70, shows indications of deriving from sources containing distinct but low proportions of both the sediment melt and fluid component. Although full trace element data are not available for the primitive Bogoslof sample, it was included in this study on the assumption that it derives from deep portions of the arc which were not strongly enriched in fluid-mobile slab components.

## 3. Analytical methods

Samples were prepared by conventional $HF:HClO_4$ digestion from which completely clear

solutions were obtained. Lithium was purified with a single step of cation exchange chromatography, using a mixture of methanol and $HNO_3$ in 12 ml of AG 50w-x8 resin. Lithium isotope ratios were measured in solutions of approximately 100 ppb Li by multiple collector magnetic sector ICP

Table 1
Elemental and Li isotope data from magmatic arc lavas

| Sample | Locality | $\delta^7Li$ | $SiO_2$ (wt%) | MgO (wt%) | $K_2O$ (wt%) | Li (ppm) | B/Be |
|---|---|---|---|---|---|---|---|
| | **Kurile arc** | | | | | | |
| 8322/3[a] | Onekotan | +4.2 | 64.7 | 1.93 | 1.31 | 16 | 79.0 |
| | replicate | +3.9 | | | | | |
| B-17-642 | Iturup | +4.9 | 59.6 | 3.11 | 0.63 | 10 | 42.4 |
| 111B | Urup | +3.1 | 60.7 | 3.23 | 1.01 | 11 | 42.0 |
| PARA-16-1 | Paramushir | +2.4 | 53.0 | 3.97 | 0.86 | – | 31.0 |
| B-11-556 | Raikoke | +4.5 | 55.7 | 3.41 | 1.32 | 11 | 19.6 |
| B-11-504[a] | Makanru | +7.4 | 55.7 | 5.09 | 1.61 | – | 10.9 |
| | replicate | +6.7 | | | | | |
| B-11-74/1[a] | submarine | +3.7 | 50.9 | 5.21 | 1.65 | – | 12.5 |
| B-11-75/4[a] | Avos | +3.2 | 52.2 | 4.47 | 1.58 | – | 12.2 |
| B-11-527 | Chirinkotan | +3.2 | 56.3 | 2.80 | 1.95 | – | 14.6 |
| B-17-34/1 | Iturup | +4.7 | 57.8 | 3.88 | 1.95 | – | 11.2 |
| K-8 | Alaid | +2.9 | 50.5 | 3.97 | 1.81 | 10 | 14.4 |
| B-11-72/3[a] | Belyankin | +3.8 | 48.0 | 5.24 | 1.60 | – | 8.4 |
| | **Sunda arc** | | | | | | |
| GU1 | Guntur | +3.5 | 50.0 | 5.91 | 0.33 | 5.0 | 9.4 |
| GU2 | Guntur | +3.7 | 61.2 | 2.97 | 1.85 | 17.8 | 51 |
| GU3 | Guntur | +2.2 | 63.4 | 2.54 | 2.15 | 20.5 | 49 |
| GU5 | Guntur | +4.2 | 51.6 | 4.40 | 0.51 | 5.6 | 12 |
| GU10 | Guntur | +2.8 | 58.4 | 3.19 | 1.48 | 13.9 | 34 |
| Ca22 | Cereme | +2.4 | 54.8 | 7.08 | 1.48 | 12.3 | 19.4 |
| | replicate | +2.7 | | | | | |
| R15 | Ringgit–Beser | +4.8 | 43.9 | 18.1 | 3.88 | – | 4.7 |
| R27 | Ringgit–Beser | +4.5 | 44.9 | 10.0 | 5.76 | – | 1.4 |
| R36 | Ringgit–Beser | +5.0 | 45.1 | 4.12 | 4.14 | – | 0.8 |
| R45 | Ringgit–Beser | +4.7 | 45.5 | 15.3 | 2.79 | – | 4.9 |
| R59 | Ringgit–Beser | +0.9 | 46.9 | 5.92 | 0.98 | 7.5 | 12.6 |
| K7 | Keli–Mutu | +4.3 | 59.8 | 3.02 | 1.70 | 16.8 | 104 |
| K22 | Keli–Mutu | +2.3 | 61.4 | 2.84 | 1.75 | 17.9 | 109 |
| | replicate | +2.5 | | | | | |
| K26 | Keli–Mutu | +3.0 | 54.9 | 4.20 | 1.01 | 11.6 | 74 |
| K30 | Keli–Mutu | +4.8 | 51.9 | 5.53 | 0.86 | 7.8 | 35 |
| K33 | Keli–Mutu | +5.1 | 63.4 | 1.80 | 1.56 | 16.2 | 44 |
| L10 | Lewitobi | +2.8 | 59.9 | 3.32 | 1.42 | 10.8 | 23 |
| L29 | Lewitobi | +4.4 | 56.2 | 4.11 | 0.80 | 7.2 | 23 |
| M19 | Mandiri | +3.9 | 48.3 | 4.67 | 1.14 | 7.0 | 6.2 |
| M20 | Mandiri | +3.9 | 56.1 | 2.87 | 2.50 | 10.5 | 7.3 |
| | **Aleutian arc** | | | | | | |
| 1927 | Bogoslof | +2.3 | 46.0 | 5.40 | 1.60 | 5.0 | 3.3[b] |
| Qaf-70 | Umnak | +2.8 | 51.4 | 5.13 | 0.66 | 9.79 | 24 |
| LUM-17 | Recheshnoi | +3.9 | 57.8 | 3.98 | 1.33 | 22.6 | 32 |
| LUM-21 | Recheshnoi | +3.2 | 50.1 | 10.1 | 0.86 | 9.22 | 8.7 |

Replicates are separate digestions of individual samples; major element data and B/Be (all samples), and Li concentrations (Aleutian samples) are literature data [13,14,18,20–22,26,49]. – = not analyzed

[a] Sample belonging to the Onkeotan-region cross-arc traverse [14]

[b] Value based on estimated B content of 3 ppm

mass spectrometry (MC-ICP-MS) using the technique of Tomascak et al. [24]. Plasma-specific interferences, such as $^{12}C^{2+}$ on $^{6}Li^{+}$, have not been observed with this instrument. Measurements were made at the Carnegie Institution of Washington, utilizing a VG Plasma 54-30 with a Cetac MCN-6000 desolvating nebulizer. Each sample analysis was bracketed by an analysis of a solution of the L-SVEC Li standard ($^{7}Li/^{6}Li = 12.02$) [25]. Early measurements using this technique established a conservative analytical uncertainty of ± 1.1‰ based on multiple duplicate analyses and the analysis of samples in replicate preparations. Since that time, however, minor modifications of the method and improved instrument performance yield external precision better than ± 1.0‰ (all statistics 2σ population).

Lithium concentrations were determined by ICP-AES using the JY-70 instrument at the Carnegie Institution of Washington (Washington, DC, USA) [26]. For the concentration range examined, uncertainties on duplicate analyses averaged 5%.

## 4. Results

Save for one sample (B-11-504;+7.4‰), the Kurile lavas define a narrow range of $\delta^{7}Li$, from +2.4 to +4.9 (Table 1). The Sunda lavas also define a narrow range of $\delta^{7}Li$, from +2.1 to +5.1, save for one sample (R59;+0.9‰). All four samples from the Aleutian arc define a similarly narrow spread in $\delta^{7}Li$ (+2.3 to +3.9). These isotopic compositions overlap the accepted range for MORB. The samples have a wide range in trace element concentrations, but there is no correlation observed between elemental indicators such as B/Be or Ba/La and $\delta^{7}Li$ (Fig. 1).

The one aberrant sample from the Sunda arc (R59: Ringgit–Beser) has the highest Ba/La, B/Nb, and Pb/Ce, and lowest $^{87}Sr/^{86}Sr$ of the samples examined from that locality, although not anomalously so. The one apparent outlier among the Kurile data (B-11-504: Makanru) has intermediate major element contents and B/Nb and B/Be compared to other samples from the arc. Hence, these samples do not show compositional
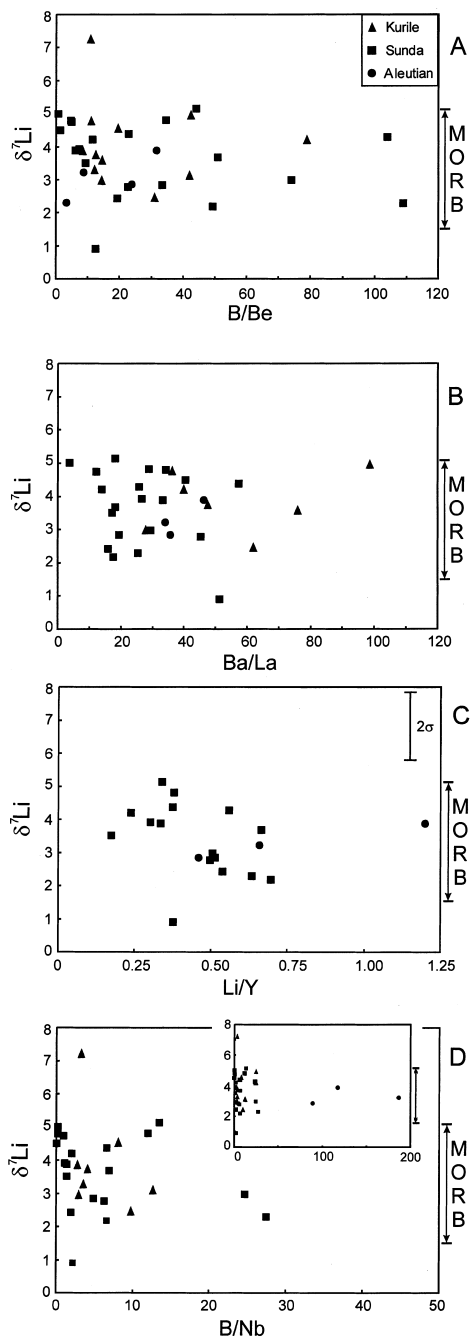


Fig. 1. Lithium isotope data for samples of the three arcs of this study plotted against conventional indicators of slab enrichment. (A) B/Be, (B) Ba/La, (C) Li/Y, (D) B/Nb (inset shows high B/Nb Aleutian samples). The range of Li isotopes in MORB [2–4] is shown for comparison in each figure. Error bar applies equally to each plot.
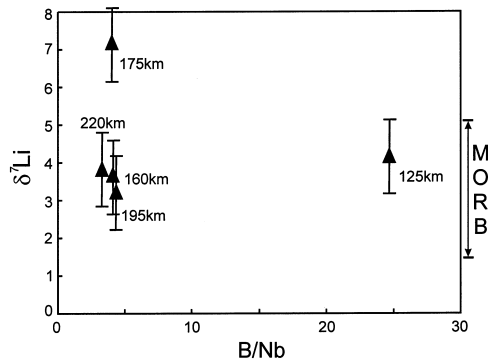
Fig. 2. Compositions of Kurile lavas from the Onekotan-area cross-arc transect. Depths to the subducting Pacific slab from [13] are noted for each. The lack of correlation in this cross-arc subset of samples further underscores the decoupling of Li and classical fluid-mobile element slab indicators, like B, in these arcs.



Fig. 4. Comparison of Li isotope compositions from Central American lavas (calc–alkaline samples from Panama: [10]; all others: [11]). Correlation between Li isotopes and trace elements in these samples is weak or absent. In particular, the samples with the strongest slab Li signature from Panama have MORB-like B/Be.

peculiarities that might allow their unusual Li isotope compositions to be explained easily.

It can be argued that comparison of lavas from along-arc volcanoes could disguise specific variations in elemental transfer related to variations in sediment composition and other factors. However, the same lack of correlation between $\delta^7Li$ and elemental systematics holds for samples from strictly across-arc segments, as well (e.g., at Onekotan, Kuriles, and among the Aleutian samples Fig. 2).

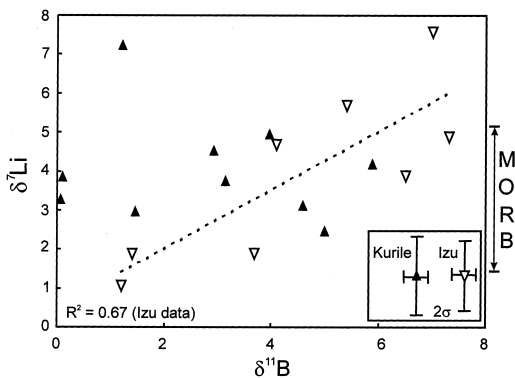The Li isotope compositions of lavas from



Fig. 3. Comparison between B [3,13] and Li isotope compositions of lavas from the Kurile and Izu arcs. Linear regression through the eight Izu data (dashed line) yields a correlation coefficient of 0.67. The Kurile data show no correlation. Equivalent relations hold when Li isotopes are plotted against trace element ratios or slab depth.
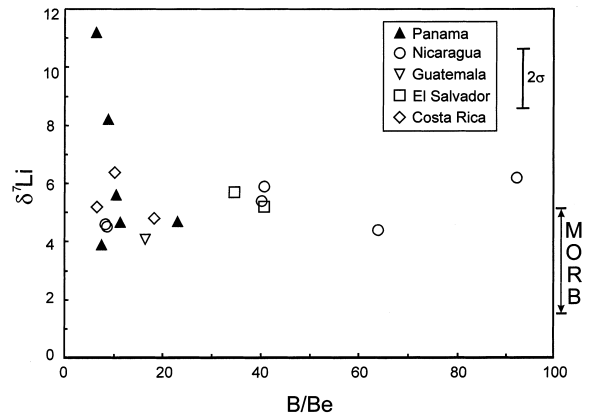
these three arcs contrast somewhat with the findings of Moriguti and Nakamura [3] (Izu arc Fig. 3), as well with some of the findings of Chan et al. [11] (specifically Nicaragua Fig. 4). In these studies the lavas with greatest enrichment in fluid-mobile elements had $\delta^7Li > MORB$, and samples showed apparent correlations between Li isotopes and B/Be, Li/Y. Neither of these studies included true across-arc sampling, though. For instance, although Izu samples represent a progression from shallow to deep slab depths, the individual volcanic centers spread over ~120 km of the strike of the arc, and therefore could have important differences in the nature of subducted sediment.

## 5. Discussion

### 5.1. Factors influencing slab–mantle Li transfer

The lavas studied here show no evidence that their Li isotopes have been influenced by the presence of subducted components. Several factors may influence the magnitude of Li release from slabs. We consider some of these below, with reference to the arcs in this study.

The upper surface of a subducting slab is a

mixture of mantling sediments on low-temperature altered oceanic crust. Where sediments are being subducted, from a Li budgetary standpoint, it may be important to understand the breakdown of components that are generally Li-poor (carbonate and silicate oozes with $< \sim 2$ ppm Li [27]) and those which should have Li abundances significantly greater than MORB (any sediment enriched in hydrous silicates). The estimated amount of sediment being subducted in each of the arcs examined here, in terms of thickness of the sediment column, is fairly similar (300–500 m) [12].

The altered ocean crust portion of the slab is characterized by Li abundance far greater than unaltered MORB ($2–10\times$[2]). It is well documented that during reaction with seawater at temperatures below $\sim 300°C$ basalt gains Li as secondary Mg-silicates replace original igneous minerals [28,29]. Additionally, the Li abundance of altered oceanic crust correlates with age of exposure on the sea floor [2], such that crust older than 50 Myr has uniformly higher Li abundances ($> 50$ ppm) than crust of 1–10 Myr ($< 20$ ppm). Hence, the age of subducting crust may play a

role in the Li budget of arcs. Older crust, by this proposition, may be more 'fertile' in terms of mass of slab Li that may be removed.

In instances of 'hot' subduction (the subduction of young, warm crust, or spreading ridges) a proportion of the slab fluid-mobile element budget is expended in the forearc. Thus lavas from 'hot' subduction zones may show lower overall elemental evidence for slab contribution [30]. Such a tectonic regime does not prevail in the arcs studied here, and in these suites it is clear that slab fluids/melts have reached the respective zones of melting in the subarc mantle from the systematic enrichments in, for example, B/Be, Pb/Ce, Sb/Th, of these lavas. In these arcs it is therefore not feasible to call upon total loss of slab Li in the forearc to explain the absence of slab Li isotope signatures in the lavas.

Two possible explanations for the lack of correlation between concentrations of other fluid-mobile elements and Li isotopes in these samples are: (1) the fluids were Li-poor, such that slab Li was largely retained in the slab and its fate was determined by much deeper processes not affecting arc
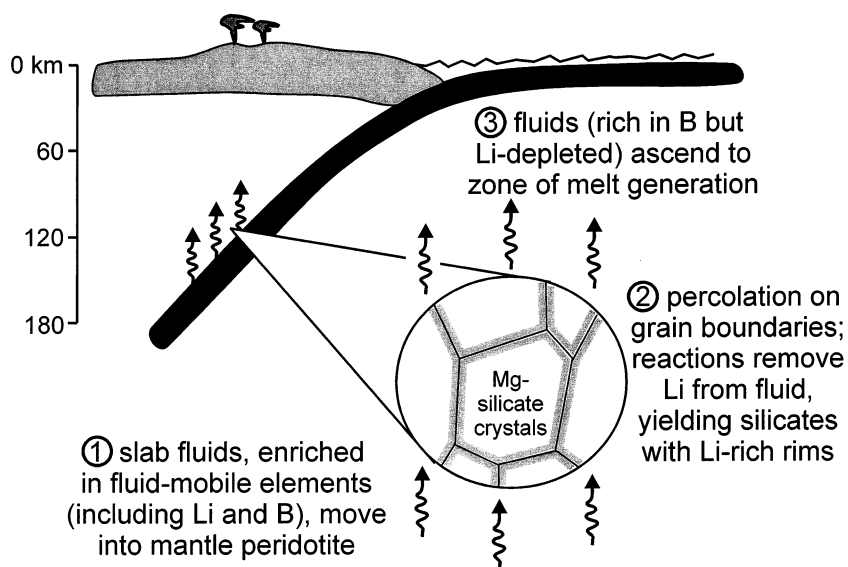


Fig. 5. Schematic illustration of proposed fluid–mantle reaction mechanism for decoupling Li and B in arcs. Initial fluid released from slab sources is enriched in both Li and B, but during transit through mantle peridotite Li is partitioned favorably into Mg-silicates, whereas B has little affinity for the solid. As a result, the subarc mantle acquires an isotopically heavy Li signature whereas arc lavas have fluid-mobile element enrichment and Li isotope signatures of ambient MORB mantle.

magmatism; (2) the fluids contained Li, but it was removed during fluid–mantle interaction en route to the zone of melting (Fig. 5). As there has been no comprehensive consideration of the Li–B abundances of slab fluids, it is not currently feasible to differentiate unequivocally between processes that fractionate Li from B on the slab from those in which these elements are decoupled in the mantle.

## 5.2. Comparison among arcs

Aside from this study, Li isotope data have only been published from three magmatic arcs: separate segments of the Central American arc [10,11], and the Izu arc [3]. The overwhelming geological difference between the arcs of this study and the Central American arc in Panama relates to thermal state of the subduction zones. Tomascak et al. [10] suggested that 'hot' subduction significantly influenced the release of slab Li previously entrained in the subarc mantle, thus producing the Li–B decoupling seen among lavas of different ages. If this interpretation is accurate, then one extension of it would be that in 'normal' subduction zones $\delta^7$Li and B/Be might commonly show no correlation. Indeed, this is demonstrated in the oldest Panama lavas, generated before the steep increase in heat flow associated with ridge subduction. This conclusion is satisfied by the data for the Kurile, Sunda and Aleutian arcs, where crust of at least moderate antiquity is being subducted.

Chan et al. [11] presented Li isotope compositions of one lava from Guatemala, two from El Salvador and three from Costa Rica. The data show no significant correlation between $\delta^7$Li and B/Be (Fig. 4). Although these data sets are too small to allow for a complete assessment, they are in general accord with what we see in the more complete arc suites of this study. The Costa Rica samples appear to follow the trend of the younger Panama lavas, which is consistent with their proximity to the region of elevated heat flow centered in northwestern Panama.

Five samples from Nicaragua (the composition of a sixth sample, from Momotombo, was left out of their assessment [11]) do not form a viable cross-arc section, but do show a correlation between small $\delta^7$Li variations (1.7‰ total variation) and elemental indicators of slab fluids (Fig. 4). Note that, within error, these $\delta^7$Li variations fall within the range of MORB compositions, although our understanding of these rocks is as of yet incomplete.

There is a modest correlation of Li isotopes and, for example, B/Be, in the Izu arc. Given the geological parallel between Izu and Kurile (e.g., age of subducting crust, similarity of incoming sediments), it would be expected that the light element budgets of the two arcs would be quite similar (Fig. 3). Indeed the inferences from other elemental and isotope systematics from these arcs suggest slab components dominated by altered ocean crust with only minor sediment influence [13,31].

Although the number of measurements limit the scope to which a difference can be discerned between the two sets of data, possible explanations for why Izu and Kurile might show such distinct B–Li trends include: (1) preferential retention of Li in the slab in the Kuriles; (2) different fluid flow regimes in the subarc mantle.

Natural and experimental constraints suggest that slab fluids are enriched in Li and B [26,32]. Abundances of Li and B (and B/Li) are quite variable among minerals likely to be important in subducting slabs [33]. Staurolite is the only potentially widespread mineral with broad stability under subarc conditions [34] that might form from the metamorphism of subducted pelagic sediments and provide a sink with high Li/B [35,36]. Although both trace element abundance and stability data are very sparse for this mineral under these conditions, without a better understanding of mineral stability and B/Li partitioning under relevant conditions it is not currently possible to rule out a mineralogical control that could retard Li release with B in slab fluids.

At subarc pressures, the transfer of slab-derived fluids upward into peridotite might generally be assumed to be a grain-boundary (percolation) process, although the velocity of fluid flow is apparently fairly high [37]. Significant exchange may occur between fluids and mantle minerals. Whereas Li contents of Mg-rich mantle silicates are sig-

nificant (1–2 ppm) [26,38], fluid percolation would result in a chromatographic exchange, and this could obscure the slab Li signature of the fluids. In contrast, if fluid/rock ratios are very high (perhaps requiring fracture flow), reaction between fluids and wall rocks would be much more limited. This would provide a means of moving fluids with slab B and Li into the region of melting without the fluid–rock reactions that have been interpreted to preferentially remove slab Li in Panama [10]. It is generally accepted that fracture flow is important in fluid transmission at lower crustal depths [39]. It is clear from veined xenoliths from the subarc mantle [40] that fluid/melt flow through fractures, although perhaps on a small spatial scale, is in some cases an important process even at these high pressures. Nonetheless, the predictability of where one flow regime dominates over another is currently entirely speculative.

## 5.3. Fate of exported crustal Li in the mantle

There are several possible fates for light elements carried by slab-derived fluids or melts to the subarc mantle. Tomascak et al. [10] argued that decoupled Li–B relations in Panama lavas resulted from chromatographic separation of B from Li during fluid transit through the subarc mantle en route to the zone of arc lava generation, consistent with experimental fluid–crystal partitioning [41]. The effects of Li metasomatism in the subarc mantle are demonstrated by in situ measurements of silicates in eclogites and high-pressure peridotites [42–44], and of subduction-related pyroxenites [7], substantiating that Li may be removed from a fluid phase by reaction with mantle silicates. Evidence for elemental decoupling during fluid–mantle reaction in the subarc regime is also manifest in the oxygen isotope compositions of minerals from lavas in Kamchatka [43].

Chromatographic effects would tend to be compensated for by large slab fluid fluxes, as suggested in the previous section. That is to say, the mantle 'column' would tend to be flushed of B as well as Li with sufficient throughput of fluid. This would tend to yield lavas with consonant Li–

B elemental and $\delta^7$Li–B systematics, as seen in the Izu arc [3].

In cases where fluid flux from the slab is restricted, liberation of slab Li from the chromatographic column would be diminished. This leads to the inexorable entrainment of exogene (slab) Li, isotopically heavier than ambient MORB, in mantle peridotite. This scenario would account for arc lavas with rather invariant, broadly MORB-like $\delta^7$Li over a large distance from arc front to back-arc.

Whether Li is retained in the slab in significant proportion or trapped in the subarc mantle, the end result is the transfer of isotopically heavy Li from near the Earth's surface to one or another part of the mantle. Over time this suggests the development of isotopically distinct regions, unless this material is efficiently mixed.

After components enriched in isotopically heavy Li have been withdrawn during subduction processing, what is the isotopic composition of the residue that carries on into the asthenosphere? Isotopically light Li in Alpine eclogites [9] suggests that dehydration of altered ocean crust and sediments may yield isotopically light residue. Similar results are apparent for B isotopes in subduction zone metamorphic minerals [45]. These results suggest that a potentially large volume of subducted material, after undergoing dehydration, is delivered to deeper parts of the mantle enriched in the respective lighter isotopes of these elements. Interestingly, early studies of ocean island basalts [46–48] do not indicate that OIB are in general strongly isotopically fractionated relative to MORB.

## 6. Summary

Consistent, MORB-like Li isotopic compositions of lavas from three globally dispersed and tectonically dissimilar oceanic arcs suggest a common controlling factor. The lavas show extreme variations in the degree of incorporation of fluid/melt slab components, as indicated by trace element ratios such as B/Be, B/Nb, Ba/La, Pb/Ce and Li/Y. There is no correlation between any of these indicators and Li isotopes. The most

plausible interpretation is that Li released by the subducting slab is removed from fluids/melts during transit through peridotite prior to reaching the ultimate region of melt generation in the sub-arc mantle, although the formation of high Li/B minerals in the subducting slab cannot be entirely ruled out. Alternate explanations are required for the apparent correlation in the elemental and isotopic data from the Izu arc.

The data from the Kurile, Sunda and Aleutian arcs suggest that significant volumes of upper mantle become isotopically heavier than ambient MORB-mantle through time, and that such material may be recovered in, for example, lithospheric mantle xenoliths.

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