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Lithium abundance and isotope systematics of forearc serpentinites, Conical Seamount, Mariana forearc: Insights into the mechanics of slab-mantle exchange during subduction

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Variable lithium contents and contrasting Li isotopic signatures are evident in the serpentinite muds and clasts extruded at Conical Seamount in the Mariana forearc. The muds have high Li contents compared to mantle values (3–7 ppm) and a mean $\delta^7\text{Li}$ value of $\sim+6\%$. The clasts are generally lower in Li, and $\delta^7\text{Li}$ varies from $-6\%$ to $+10\%$, with higher $\delta^7\text{Li}$ correlating broadly to higher lithium contents. The diverse $\delta^7\text{Li}$ in the serpentinite clasts suggests Li exchanges between mantle rocks and evolving slab-derived fluids from different depths, producing a subarc mantle that is zoned in terms of Li abundances and $\delta^7\text{Li}$. Mariana forearc Li isotopic signatures reach values as high as those reported in Mariana arc lavas, but neither Mariana lavas nor lavas from other “mature” arcs show the variability observed in the serpentinites. Although elevated serpentinite Li contents indicate forearc releases of Li, large differences in $\delta^7\text{Li}$ are not evident in the slab outputs at forearc versus arc depths in the Marianas, despite evidence for changes in other alkaline species (e.g., Ba, Sr, K). It is thus possible that the Li sampled by Mariana arc volcanoes is in large part Li which was released in the forearc and transported in the mantle via convection to arc depths, as has been proposed to explain B isotopic variations [Straub and Layne, 2002]. The uniform $\delta^7\text{Li}$ signatures observed in “mature” volcanic arcs [Tomascak et al., 2002] are consistent with higher overall fluxes of slab fluids, which generate larger melting anomalies, including both modified and nonmodified mantle wedge domains. High or low $\delta^7\text{Li}$ in lavas from anomalous arcs (e.g., Panama [Tomascak et al., 2000]) may indicate that the volumes of mantle sampled in these magmatic events are smaller and thus more likely to reflect the signatures of hydrated “plums” [e.g., Allègre and Turcotte, 1986; Phipps Morgan and Morgan, 1999] with extremely high or low $\delta^7\text{Li}$. 
1. Introduction

The “slab input” to the mantle sources of arc lavas is a chemically complex flux within which a number of components have been identified: melts of subducted sediment [Plank and Langmuir, 1993; Elliott et al., 1997], fluids from basaltic crust [Miller et al., 1994; Ishikawa and Nakamura, 1994; Class et al., 2000], melts of basaltic crust [Kepezhinskas and Defant, 1996] and fluids derived from subducted sediment [Class et al., 2000]. While these different components can be recognized on discrimination diagrams, it is difficult to quantify their relative roles, as we have no physical or geochemical descriptions of them; i.e., if a fluid from sediment is involved, what is the overall makeup of this fluid phase (i.e., proportions of H2O, CO2, SO2, halogens; pH; fO2) and what elements and/or chemical species does it transport at the depths of arc volcanic root zones? In the Mariana subduction system we have an opportunity to assess one particular slab outflux: an H2O-dominated fluid release at low temperatures, which is absorbed into the mantle wedge via serpentinization reactions, and is thus measurable through analysis of the diapiric serpentinites erupting in the outer forearc region of the Mariana arc. This flux has been shown to mobilize a limited menu of “fluid mobile” species, which, interestingly, do not include elements such as Ba and U, that are normally used to fingerprint slab influences [Pearce and Peate, 1995; Elliott et al., 1997; see also Savov et al., 2000, 2002; Morris and Ryan, 2003].

Lithium is an element that appears to be mobile in forearc settings, and it is unique among mobile elements in that it partitions well into olivine and other Mg silicates [Ryan and Langmuir, 1987; Brenan et al., 1998a, 1998b; Seitz and Woodland, 2000]. Lithium abundance and isotope systematics may thus be able to provide a more detailed picture of how slab fluids interact with the mantle in forearc settings. Lithium isotopes show strong fractionations during solid-fluid exchanges due to the large mass difference between 6Li and 7Li [e.g., Chan and Edmond, 1988], and should thus allow us to assess how Li is moved from slab to mantle at arc or forearc depths. We report below on Li abundance and Li isotope data collected on serpentinite muds and serpentinized ultramafic rocks from the Conical Seamount, an active serpentinite mud volcano situated ~29 km above the downslabing in the Mariana forearc [Fryer, 1992].

2. Geologic Setting and Sample Selection

The Conical Seamount lies at approximately 19°31’N Latitude, 146°40’W Longitude, at ~3000 m water depth, ~90 km inboard of the Mariana trench (Figure 1). All the forearc seamounts of the Mariana subduction system lie within zones of extensional faulting which run perpendicular to the strike of the trench. The seamount consists of sequences of serpentinite mudflows, and these flows include entrained clasts of highly serpentinized harzburgites and dunites [Hussong and Fryer, 1985; Fryer et al., 1990; Fryer, 1992, 2002]. Mudflow activity is driven by the upwelling of an evolved, highly alkaline (pH 12.6), low-chlorinity (less than half that of seawater) pore fluid that originates from the dehydration of the subducting slab and is responsible for serpentinization reactions at depth. This fluid, sampled as pore waters in


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the uppermost portion of the seamount (1–300 meters below seafloor (mbsf)), also has distinctive trace element signatures, including highly elevated B concentrations (~42 ppm, ~10x seawater) and Li contents (at ~11 ppb) that are more than three orders of magnitude lower than seawater [Fryer et al., 1985; Fryer and Fryer, 1987; Mottl, 1992; Mottl et al., 2003].

Figure 1. Map of the Mariana forearc region, with close-up of the Conical Seamount showing the location of Sites 779 and 780. From Fryer [1992].
During the Ocean Drilling Program (ODP) Leg 125, three sites on Conical Seamount were drilled: the summit (Site 780) and two flank sites (Sites 777 and 779; Figure 1 inset). Drill core from Holes 780C and 779A provide the longest sequences of serpentinite muds and clasts, and also include fragments of basaltic crustal rocks, as well as small pieces of blueschist-facies meta-mafic rocks which are probably derived from the downgoing plate [Fryer and Fryer, 1987; Fryer, 1992; Maekawa et al., 1992, 1995]. Serpentinites (i.e., clasts and matrix collectively unless specified otherwise) from Site 780 are in intimate association with anomalous pore waters to within 3 m of the seafloor. Serpentinites from Site 779 are in contact with higher chlorinity pore waters, which show evidence for exchange with seawater, but preserve the high pH characteristics of the upwelling fluid at depths below ~100 mbsf [Fryer, 1992; Mottl, 1992].

Samples of the serpentinite muds were selected to examine the Li and Li isotope systematics of the evolving, slab-derived fluid, as data for B isotopes and other tracers suggest that the muds are in chemical equilibrium with the pore waters [Benton et al., 2001; Haggerty, 1991; Haggerty and Chaudhuri, 1992; Mottl, 1992; Mottl et al., 2003]. Samples of the entrained ultramafic clasts were examined in search of deeper-seated Li isotopic signatures, which might be more representative of conditions closer to the slab-mantle interface. Most of our samples are highly serpentinized (>60% serpentinite) with loss on ignition (LOI) values between 8% and 24%. As pH, Sr isotope, and B isotope results indicate the influence of infiltrating seawater in shallow portions of Sites 779 and 780 (see above), we focused our sampling on deeper segments of cores, and followed the same protocols for sample selection and preparation as had been used for B isotopes (see below). As was the case with B and B isotopes, Li concentrations and Li isotope ratios appear unaffected by seawater in the deeper core segments at both sites. Shallower core sections show Li concentration and Li isotope variations similar to those found deeper, suggesting that overall, the influence of seawater may be negligible.

3. Methods

We chose samples for analysis from both Site 779 (Holes A and B) and Site 780 (Holes C and D; Figure 1). Clast samples were selected from the interiors of relatively vein-free core segments, on the presumption that the interiors are less likely to suffer late-stage exchanges with seawater. However, it turned out to be impossible to avoid finer veins, so many of our samples included veined materials. Both the matrix and clast samples consisted of chrysotile ± lizardite or antigorite [Mottl, 1992; Fryer, 1992; Heling and Schwarz, 1992; Lagabrielle et al., 1992; Saboda et al., 1992]. Matrix samples were ground with an agate mortar and pestle and then washed with deionized water to remove salts from pore waters [Spivack and Edmond, 1987]. Clast samples were crushed, washed in deionized water, and powdered in a ball mill using an alumina vial dedicated to serpentinite samples.

Samples analyzed for Li abundances were dissolved using an HF:HClO₄ digestion technique, and analyzed by standard additions methods via Direct Current Plasma emission spectrometry (DCP) (see Ryan and Langmuir [1987] for details on the method). A subset of the samples was analyzed for Li by isotope dilution mass spectrometry (IDMS) (see Table 1). Agreement between DCP and IDMS Li data is within the ±5% precision of the DCP analyses.

Samples for Li isotope determinations were prepared via an HF:HNO₃:HClO₄ digestion, followed by a final dry-down in concentrated HNO₃, which was necessary to decompose abundant Mg(ClO₄)₂ generated in the breakdown of these Mg-rich rocks. Mg-perchlorates have a limited solubility in the 0.66 M HNO₃/33% methanol solutions loaded onto cation columns for Li elution, and could be observed as an immiscible liquid when present. Lithium isotope measurements on samples with Mg-perchlorate residues were anomalously high, suggesting some fractionation of the isotopes occurred when it was present. The addition of strong HNO₃ followed by a hard dry-down at ~160°C resulted in clear solutions for all such samples, though in a few cases multiple dry-downs were necessary to decompose all of the Mg-perchlorates.

For isotopic analysis, Li was isolated by ion-exchange chromatography using the methanol-HNO₃ method described by Tomascak et al. [1999a], and the final solutions were diluted to ~100 ng Li/ml for analysis. Lithium isotope measurements were made on the VG P-54 multiple-collector magnetic sector ICP-MS at the Department of Terrestrial Magnetism according to procedures outlined by Tomascak et al. [1999b]. Each sample was measured a minimum of three times, and the measurements were averaged. Duplicates of several of our samples were prepared and analyzed as a further check on precision (see Table 1). On the basis of the total
errors of our sample measurements, and duplicate analyses of samples, our precision was at least as good as the ±1\% (2σ) level reported for the ICP-MS method in the past [e.g., Tomascak et al., 1999b, 2000].

4. Results

Lithium abundance and Li isotope data for the Conical Seamount and relevant reference samples are presented in Table 1. Lithium concentrations in the serpentinized ultramafic clasts are quite variable, ranging from 0.9–18.9 ppm. The serpentinite matrix samples range from 1–8 ppm Li (with one outlier at 26.3 ppm), and are less variable in Li content (Figure 2). Lithium contents in Site 779 matrix samples appear to be lower than those from Site 780 (1–4 ppm versus 4–8 ppm, respectively; Figure 2). The very high Li concentration in sample 779A-36R-2, 132–134, the deepest sample analyzed (306 mbsf), probably cannot be generated purely via equilibrium exchange of serpentine with the associated, higher Li pore waters (0.2–0.8 ppm Li, higher than seawater [see Mottl, 1992]), especially given the low Li contents of other mud samples in contact with these fluids. The Li content in this sample may thus reflect the admixture of fine-grained mafic materials with higher Li and/or a higher affinity for Li during solid/fluid exchange [Benton, 1997; see also Guggino et al., 2002; Savov, 2004].

Lithium concentrations show no clear relationship to LOI in our samples, or to the abundances of other fluid-mobile, incompatible trace elements (Figure 3). The serpentine matrix samples show a general positive variation relative to boron contents, but with several outliers at very high B or Li abundances. The cause for this diversity may be that, as noted above, mud samples may contain variable amounts of fine grained, altered mafic material (either blueschist-grade crustal material from the slab, or material from the overriding
crust), which could affect the systematics of these elements differently [Benton, 1997; Guggino et al., 2002; Savov, 2004].

[13] Li isotopic variations in the clasts and muds contrast markedly. The serpentinite muds span a limited range of $\delta^{7}\text{Li}$ (+4 to +8%), with a mean value near +6%. The serpentinized clasts vary widely in $\delta^{7}\text{Li}$, from −6% to +10% (Figure 4). This variation is not related to LOI or abundances of other mobile elements (Figure 5), but does show a broad relationship to Li content, with the higher Li clasts associated with generally higher $\delta^{7}\text{Li}$ values, and those samples with Li contents <5 ppm covering nearly the entire range of $\delta^{7}\text{Li}$ values observed (Figure 6).

5. Discussion

5.1. Origins of Li Distribution and $\delta^{7}\text{Li}$ Signatures in Conical Serpentinites

[14] Lithium concentrations in the Leg 125 serpentinites are generally elevated relative to their harzburgite or dunite protoliths [Ryan and Langmuir, 1987; Seitz and Woodland, 2000]. Interestingly, Li abundances are quite variable in the Leg 125 samples analyzed. The serpentinized clasts show the greatest degree of variation in this regard (up to 18.9 ppm Li) and also include a number of samples that approach the Li contents of depleted ultramafic...
rocks (i.e., \(1–2\) ppm [see Ryan and Langmuir, 1987; Seitz and Woodland, 2000]). Lithium contents in the serpentinite muds are, by contrast, generally more consistent. It is possible that Li contents in matrix serpentines reflect in some way the equilibration of these Mg-silicates with their associated pore waters: the upwelling, evolved slab-derived fluids at summit Site 780, and the seawater modified fluids found at flank Site 779.

Lithium partitions strongly into serpentine under low-temperature conditions as seen with other sheet silicates [Seyfried et al., 1984; Scambelluri et al., 2004]. Scambelluri et al. [2004] suggest a \(D_{\text{serpentine/liquid}}\) of \(~3.5\) for dehydration reactions in Alpine serpentinites, and the mud/fluid ratio of Li concentrations between the Site 779 muds and pore waters are consistent with such a \(D\) value. The much higher mud/fluid ratio for Li at Site 780 requires progressive removal of Li from the upwelling fluids into serpentine, producing very Li-depleted pore waters near the surface.

The large variation in Li contents and \(\delta^7\text{Li}\) among the serpentinitized clast samples argues against both simple models of equilibration with associated pore waters, or Rayleigh-style models for progressive removal. The ready uptake of Li by serpentine and other sheet silicates under low-temperature (<300°C) conditions [Seyfried et al., 1984, 1998] means that Li from vein fluids will be

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**Figure 4.** Plot of \(\delta^7\text{Li}\) for Leg 125 serpentinites versus depth in core.

**Figure 5.** Plots of (a) \(\delta^7\text{Li}\) versus LOI; (b) \(\delta^7\text{Li}\) versus K concentrations; and (c) \(\delta^7\text{Li}\) versus B concentrations for Leg 125 serpentinites. Additional data are from Benton et al. [2001] and Mattie and Ryan [1994].
incorporated rapidly by forming serpentine, creating a Li “concentration front” near the vein that diminishes rapidly with distance from the vein (Figure 7). High Li in serpentinized clasts probably indicates proximity to veins providing Li-enriched slab fluids, while low-Li serpentinized clasts indicate modification by waters from which Li has been removed during earlier fluid-rock exchanges. The result of these sorts of progressive exchanges should be markedly variable Li contents in serpentinized mantle rocks [e.g., Decitre et al., 2002].

[17] Lithium isotope systematics of the Conical serpentinites present a picture similar to that for Li abundances: the serpentinized matrix samples approach a mean $\delta^7$Li value of +6‰, while the serpentinized clast samples show substantial variation, including values both lower and higher than the $\delta^7$Li range of the matrix samples. Lithium isotope ratios in the Leg 125 serpentinite clast and matrix materials are similar to a first order to those found in oceanic serpentinites by Decitre et al. [2002]. However, data for the associated pore waters, and B isotope results on these same samples document that the role of seawater in the development of the Leg 125 serpentinites is negligible [Benton et al., 2001; Mottl, 1992; Mottl et al., 2003]. The similarity in Li isotope results for the Mariana forearc serpentinites and marine serpentinites documents that, as in the oceans, the Leg 125 samples have interacted with fluid phases that had very high $\delta^7$Li [Chan and Edmond, 1988; Chan et al., 1992, 1994].

[18] Recently reported Li isotope data for pore waters from the South Chamorro serpentinite seamount (drilled during ODP Leg 195) point to exceptionally heavy signatures, with $\delta^7$Li values greater than +40‰, suggesting fluid-serpentine fractionations of $\sim$+30‰, assuming equilibrium exchange [see Savov et al., 2002]. $\delta^7$Li values like those of the serpentinite matrix samples reflect the mean Li isotopic signature imparted on the shallow mantle wedge by evolving slab fluids. This signature has a $\delta^7$Li value lower than reported averages for the altered crustal and sedimentary constituents of downgoing slabs, which range from +8 to +14‰ [e.g., Chan et al., 1992, 1994]. The $\delta^7$Li signatures of our serpentinites are also considerably lower than the $\delta^7$Li (up to +20‰) inferred for the forearc reservoir from recent studies of eclogites and high-grade metamorphic suites, which indicate that deeply subducted materials may have very low $\delta^7$Li [Zack et al., 2003]. Specific data for the Li isotope ratios of Mariana trench sediments and altered crust are not available, so it is not clear if the serpentinites preserve Li that is different isotopically from the probable slab “infeed” to the Mariana subduction system. However, these serpentinites are consistent with the kinds of Li isotopic signatures encountered in lavas from the Mariana arc system, and in other island arcs.

Figure 6. Plot of $\delta^7$Li versus Li concentrations for Leg 125 serpentinites.
5.2. Sources of Li Isotope Heterogeneity in the Forearc Mantle

The Li isotopic diversity of the Leg 125 clasts is comparable to the in situ heterogeneity in Li isotopic compositions observed in seafloor serpentinites from the Southwest Indian Ridge [Decitre et al., 2002]. Our serpentinite clast data shows a broad correlation to Li content (i.e., higher $\delta^7$Li samples generally have higher Li abundances) and at the high end it overlaps the serpentinite mud data. However, there is a significant range in $\delta^7$Li at both the high-Li and low-Li ends of the array (i.e., samples with $>10$ ppm Li have $\delta^7$Li of $+3.5$ to $+10\%$, and samples with $<2$ ppm Li have $\delta^7$Li of $+6$ to $-6\%$; Figure 6). The pattern in Figure 6 implies that higher $\delta^7$Li clasts are produced via incorporation of slab-derived Li with a heavier Li isotopic composition, but the diversity in the data requires calling on a complex mixing process between the mantle wedge and slab-derived fluids of different compositions.

Figure 7. Sketch of a veined Mariana forearc serpentinite showing a likely pattern of Li distribution due to exchanges with vein fluids. Slab-derived fluids inject Li (red lettering), which is largely deposited in serpentine near the vein. Percolation of fluid outward from the vein forms serpentine with progressively lower Li content (brown to blue to black lettering). Subsequent fluid injections will overprint this pattern, producing serpentines with highly variable Li contents. Lithium isotope ratios in the forming serpentinite will vary on the basis of depths of fluid origin and the composition of the mantle, though high-Li samples will have higher $\delta^7$Li (see also Figure 8). Dashed circles overlain on the sketch represent the kind of sampling of this modified mantle that could occur during melting: small F melts will preferentially sample the most hydrated portions of the subarc mantle, but these portions may have either high or low $\delta^7$Li. Melting at larger values of F will average greater volumes of mantle, producing lavas with intermediate (and relatively uniform) $\delta^7$Li.

Figure 8 describes one means for generating the $\delta^7$Li variation in the clasts. Any fluid derived from the slab will carry Li with a $\delta^7$Li value significantly higher than that of the slab, as all known solid/fluid fractionation processes for Li concentrate $^7$Li in the hydrous fluid phase [Chan and Edmond, 1988; Chan et al., 1992, 1994]. The degree of Li abundance enrichment in slab-derived fluids will depend on the temperature of fluid release, as $D_{\text{solid/fluid}}$ is strongly temperature dependent between 100 and 400°C, with Li becoming more soluble where temperatures are higher [Seyfried et al., 1984, 1998]. As well, the $\delta^7$Li of slab fluids will become lower as the temperatures of fluid generation increase, because $\alpha_{Li}$ declines with increasing temperature. Thus fluids released from the slab at relatively low temperatures (i.e., at shallow slab depths) will have lower Li contents, but higher $\delta^7$Li, while fluids released at higher temperatures (i.e., greater depths) will have higher Li contents and lower $\delta^7$Li. Progressive exchanges between such slab fluids and mantle rock in the shallow forearc will produce serpentinites with variable Li concentrations (due to the high $D_{\text{serpentine/fluid}}$ [Scambelluri et al., 2004]). Lithium isotope ratios in the forming
Figure 8. Plot of $\delta^7\text{Li}$ versus Li concentrations for the Leg 125 serpentinized clast samples. The four trend lines represent possible serpentine compositions developed during progressive fluid/rock serpentinization reactions with fluids derived from deeper (Models 1 and 2) and shallower (Models 3 and 4) portions of the slab. Serpentine compositions were calculated incrementally using the equilibrium fluid/rock exchange equation [Nabelek, 1987, equation (3)]: $C_f = (C_i + NC_w)/(DN + 1)$ for Li concentrations and $R_f = [(R_i + 1000) + N(R_w + 1000))/(\alpha l_i^+N + 1)] - 1000$ for $\delta^7\text{Li}$ values, where $C_i$ represents concentrations in the fluids, $R_i$ is the $\delta^7\text{Li}$ of the rock, and $R_w$ is the $\delta^7\text{Li}$ of the fluid; $\alpha l_i^+$ is the fluid/solid distribution coefficient for Li (set at 3.5 [Scambelluri et al., 2004]), and $\alpha l_i$ is the Li isotope fractionation factor (set at 1.015, assuming higher temperatures than encountered during exchanges on the seafloor [e.g., Chan et al., 1992]). Initial fluid Li concentrations and isotope ratios were estimated on the basis of the values necessary to produce the high-Li, high-$\delta^7\text{Li}$ samples along each trend. Fluid/rock ratios begin at 1.5 for the deep fluid trends and at 2.3 for the shallow fluid trends. The Li concentration of the mantle is set at 1.5 ppm [Ryan and Langmuir, 1987; Seitz and Woodland, 2000], while mantle $\delta^7\text{Li}$ values were selected to best approximate the trends of our data. Fluid/rock ratios were reduced with each increment calculated to reflect the incorporation of fluids into forming serpentines; increment sizes were kept small so as to approximate continuous fluid/rock exchange during serpentine formation. The large range of $\delta^7\text{Li}$ in both the high-Li and low-Li serpentine clasts necessitates multiple fluid/rock exchange trajectories with fluids of different initial $\delta^7\text{Li}$ and lithium concentrations, and a mantle that is already zoned in terms of Li isotopic composition.

[21] The calculated fluid-rock exchange trajectories on Figure 8 reflect progressive serpentine formation due to the reaction of slab-derived fluids with the forearc mantle wedge. No single trajectory can explain the range of Li abundances and $\delta^7\text{Li}$ values observed in our Leg 125 clasts. However, a series of trajectories, reflecting exchanges with fluids possessing variable Li concentrations and $\delta^7\text{Li}$, consistent with the signatures of fluids released from the slab at different depths, approximates the observed variation, assuming the mantle possesses significant variability in its Li isotopic signature before exchange (i.e., that mantle horizons already existed with $\delta^7\text{Li}$ from $+6\%$ to $-6\%$).

[22] Nishio et al. [2004] has reported $\delta^7\text{Li}$ signatures for mantle xenoliths ranging from $+6\%$ to $-17\%$, and attributes the lower values to exchanges with distinct metasomatizing agents derived from slab materials subducted to great depths. Zack et al. [2003] also infers the release of slab fluids at great depths to produce eclogites with $\delta^7\text{Li}$ of $-11\%$. A low-$\delta^7\text{Li}$, deep-derived slab fluid percolating upward (i.e., down temperature) along the slab-mantle interface could react at shallower depths with upper mantle materials that have $\delta^7\text{Li}$ $\approx +3\%$ to produce solids with lower $\delta^7\text{Li}$, because the value of $\alpha l_i$ fluid/solid at the depth of this reaction will be larger than at the depth from which the fluid originated. Exchanges between deep-derived slab fluids and upper mantle materials in the forearc may be a viable mechanism for creating zones of variable $\delta^7\text{Li}$ in the mantle.

5.3. Implications for Li Isotope Systematics in Volcanic Arcs

[23] Significant heterogeneity in radiogenic isotopic signatures (i.e., $\text{Sr}/\text{Sr}$, $\text{Nd}/\text{Nd}$, U-Th-Pb) is well documented in mantle rocks [Nishio et al., 2004; Reisberg and Zindler, 1986; Reisberg et al., 1989; and references therein]. Variations in radiogenic isotope ratios within an ultramafic massif can be as great or greater than the total isotopic variation observed in mantle-derived volcanic rocks [see Reisberg et al., 1989, Figure 10]. The range of $\delta^7\text{Li}$ values in our Leg 125 clasts is larger than the total Li isotopic variation among all igneous rocks thus far examined. The highest values in our suite (at $+9.9\%$) are only slightly lower than the highest $\delta^7\text{Li}$ ever reported in an arc, $+11.2\%$ in the Panama arc segment of Central America [Tomascak et al., 2000]. So, as with radiogenic isotope systems, Li isotope ratios may record fine-scale geochemical variations in mantle

serpentinites will be related to the original $\delta^7\text{Li}$ values of the fluid and the mantle, and to the isotope fractionation factor for Li between serpentine and fluid (i.e., $\alpha l_i^+\text{fluid/serpentine}$) at the temperature (i.e., depth) of exchange.
source materials. This variation arises from multi-stage additions of exotic (in this case, slab-derived) components, and isotopic exchange under multiple P-T conditions.

[24] Modeling the Li isotope systematics of subduction zones as a simple mixture of slab-derived and mantle-derived Li, as is often done in examining isotopic variations in arcs, is problematic because of the complex manner in which slab lithium is added to the subarc mantle, and the significant redistribution of Li that occurs as a result of such additions. Straub and Layne [2002] explained unusually high $\delta^{7}\text{Li}$ values in tephra glasses from the Izu arc through mechanical inputs to subarc source regions of forearc derived, high $\delta^{11}\text{B}$ serpentinitized mantle materials via drag convection [e.g., Tatsumi, 1986]. Our Li isotope results for Conical serpentinites indicate that such a model is a permissible explanation of observed Li isotope systematics in the Mariana arc, and in other “mature” subduction systems where the observed Li isotopic variation is limited [e.g., Benton and Tera, 2000; Chan et al., 1999, 2001; Tomascak et al., 2002]. However, arcs in which Li isotopic compositions both heavier and lighter than those in the Mariana arc system are encountered (e.g., Panama [Tomascak et al., 2000]) cannot be easily explained in this manner.

[25] Perhaps the best model for understanding the Li isotopic diversity that results from slab inputs, and relating this diversity to the Li isotopic signatures of arcs, is to call upon the “plum pudding” type models used to explain mantle reservoir mixing and magmatic sampling at ocean islands and seamounts [Allegre and Turcotte, 1986; Batiza and Vanko, 1984; Phipps Morgan and Morgan, 1999]. Vein serpentine and highly hydrated ultramafic materials near veins will have high Li and variably high $\delta^{7}\text{Li}$, while the variably serpentinitized mantle between zones of veinine will have lower Li concentrations, and $\delta^{7}\text{Li}$ values ranging from those of typical upper mantle (i.e., MORB-like) to exceptionally low values, perhaps reflecting exchanges with deep slab fluids (Figure 7). If these complexly modified mantle materials convect to depth and became part of a subarc mantle source, both the hydrated higher $\delta^{7}\text{Li}$ materials, and the hydrated low- $\delta^{7}\text{Li}$ mantle rocks will be more liable to melt. Thus, at low values of melt fraction (F), either high-$\delta^{7}\text{Li}$ or low-$\delta^{7}\text{Li}$ melts (or melts consisting of mixtures of these end-member materials, dominated by the higher Li abundance end-member) might occur, as initial melts will be dominated by hydrated mantle components. As F increases, more of the mantle source melts, and proportionally less hydrated mantle material will be sampled by melting, which should shift the mean $\delta^{7}\text{Li}$ of the forming magmas away from extreme values, and closer to an average value for upper mantle rocks.

In “mature” arcs such as the Mariana subduction system, the Kuril arc and others, values for F are generally high, so $\delta^{7}\text{Li}$ approaches MORB-like values [Benton and Tera, 2000; Tomascak et al., 2002]. In anomalous arc settings, such as Panama, [e.g., Defant et al., 1991; Tomascak et al., 2000] magmatism is more sporadic, F is necessarily lower, and Li isotopic ratios may thus approach some of the more extreme values encountered in the Mariana forearc mantle.

5.4. Comparisons to B Isotope Systematics in Arcs and Implications for Li Isotopes as a “Tool” in Studies of Subduction Zones

[26] Given the differences in their solid-fluid behaviors in forearc settings, the B and Li isotopic systems provide distinctly different types of information about the slab-mantle exchange processes occurring during subduction. Boron abundances and B isotopes provide a fingerprint of the slab fluid input, while Li abundances and Li isotopes provide insights into how this fluid input modifies and hybridizes the subarc mantle. The “decoupling” of Li isotopes and B/Be systematics in Panama arc lavas reported by Tomascak et al. [2000] is consistent with the behavioral characteristics of these elements: boron tracks slab fluid inputs exclusively, while Li “sees” subduction-generated mantle heterogeneity beneath the Panamanian arc, and not just the signature of the most recent fluid inputs (Figure 9). Mantle heterogeneity beneath volcanic arcs is evident only where the “slab effect” is minimized [see Edwards et al., 1993; Lin et al., 1990]. In the case of Li, preserved mantle heterogeneity may be related to past slab-mantle exchange events, so presumably Li isotopic variations in arc lavas will only be identifiable in the case of “dying” arcs, where subduction rates and associated slab fluid inputs have diminished.

6. Conclusions

[27] Serpentinite muds from the Mariana forearc have Li isotope ratios lower overall than many probable slab materials, but similar to Mariana arc lavas. The associated serpentinitized ultramafic clasts preserve heterogeneous $\delta^{7}\text{Li}$ signatures, reflecting a complex history of exchanges between
Li-bearing, slab-derived fluids and the forearc mantle wedge. Melting beneath arcs mixes Li-enriched mantle horizons with unaltered mantle rocks, producing $\delta^7\text{Li}$ values only modestly different from those of MORBs. Only in anomalous circumstances can the Li isotope heterogeneity of the mantle be observed in the compositions of arc lavas.

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![Figure 9](attachment:figure9.png)

**Figure 9.** Plot of $\delta^7\text{Li}$ versus B/Be for arc lavas. The darkly shaded field across the diagram represents the combined $\delta^7\text{Li}$ arc data sets of Chan et al. [1999, 2001] and Tomascak et al. [2002], which constitute most of the available data on “normal” arcs, and overlaps entirely with the range for MORBs (labeled [Tomascak and Langmuir, 1999]). The symbols represent Old Group (squares) and Young Group (circles) arc lavas from Panama [Tomascak et al., 2000]. The range of $\delta^7\text{Li}$ for the Mariana forearc serpentinites is shown by the large bracket to the right of the plot. The stippled vertical field represents the range of possible $\delta^7\text{Li}$ signatures developed in the mantle wedge over time via slab fluid exchange, and the curves represent hypothetical mixing arrays between these mantle reservoirs and slab fluid, which has high B/Be, and (in most arcs) relatively MORB-like $\delta^7\text{Li}$. 
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