Boron isotope systematics of slab fluids as inferred from a serpentine seamount, Mariana forearc

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Abstract

Serpentinite clasts and muds erupted from Conical Seamount, Mariana forearc, show substantial enrichment in boron (B) and ^{11}B (δ^{11}B up to +15‰) relative to mantle values. These elevated B isotope signatures result from chemical exchange with B-rich pore fluids that are upwelling through the seamount. If the trends of decreasing δ^{11}B with slab depth shown by cross-arc magmatic suites in the Izu and Kurile arcs of the western Pacific are extended to shallow depths ($\sim$25 km), they intersect the inferred δ^{11}B of the slab-derived fluids (+13‰) at Conical Seamount. Simple mixtures of a B-rich fluid with a high δ^{11}B and B-poor mantle with a low δ^{11}B are insufficient to explain the combined forearc and arc data sets. The B isotope systematics of subduction-related rocks thus indicate that the fluids evolved from downgoing slabs are more enriched in ^{11}B than the slab materials from which they originate. Progressively lower δ^{11}B in arc lavas erupted above deep slabs reflects both the progressive depletion of ^{11}B from the slab and progressively greater inputs of mantle-derived B. This suggests that the slab releases ^{11}B-enriched fluids from the shallowest levels to depths greater than 200 km. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Boron (B) abundance and isotopic variations in island arc magmas of the western Pacific define a trend showing decreases in B abundance and δ^{11}B with increasing slab depth. This phenomenon is thought to relate to the preferential transfer of B from the slab to the mantle wedge during progressive dehydration of subducted material [1–6]. Cross-arc B abundance and B–^{10}Be systematics [7] suggest a very efficient transfer of B and like elements from the slab, through the mantle wedge, and into arc volcanics, with little B reaching depths greater than the volcanic roots of arcs. However, estimates for the total volcanic flux of B at arcs typically account for ≤ 30% of slab B inputs via subducted sediments and altered oceanic crust (AOC) [8–11]. Current models for the B isotope systematics of arcs [1,2,5,6,12] have done little to clarify the mass–balance questions about

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B, as the required 'slab fluid' component appears to derive almost all of its B from subducted ocean crust (as opposed to the B-rich sedimentary section, which also provides all subducted [10]Be). In addition, the B content and isotopic ratio of the 'mantle' end-member are not well constrained.

B abundance and isotope systematics in arcs point to a significant role for slab fluid releases in forearc regions. As forearcs are generally quiescent in terms of eruptive activity, samples of slab fluids and materials unaltered by migration through accreted sediments have not been available for study. However, at several locations in the Mariana forearc, serpentine seamounts erupt fluids and serpentine muds, with entrained serpentinized ultramafic clasts, that are mineralogically and isotopically consistent with mantle material hydrated by slab-derived fluids originating at ∼20–25 km depths [13–19]. These forearc serpentine seamounts offer a unique opportunity for the study of slab fluxes in the shallowest parts of a subduction system. We present B abundance and isotopic compositions of serpentine muds and serpentinized ultramafic clasts from Conical Seamount, an active serpentine mud volcano in the Mariana forearc, with the goal of understanding the subduction zone flux of B through the forearc region.

2. Geologic background

Conical Seamount is the most intensely studied of a number of active and inactive serpentine mud volcanoes found in the Mariana forearc [15,20–22] (Fig. 1). The seamounts occur across a broad region of the forearc some 50–120 km west of the trench axis, in a zone of extensional deformation [23]. The Mariana serpentine seamounts consist primarily of sheared, tectonized and serpentinized ultramafic rocks in a matrix of silt-sized serpentine (muds) [16]. These serpentinites possess characteristically higher $\delta^{18}O$ and somewhat lower δD than serpentinites from other marine settings, and associated authigenic carbonates show fractionated C and O ratios, consistent with interactions with fluids isotopically distinct from seawater [18,24,25]. *Alvin* dives at Conical Seamount dis-
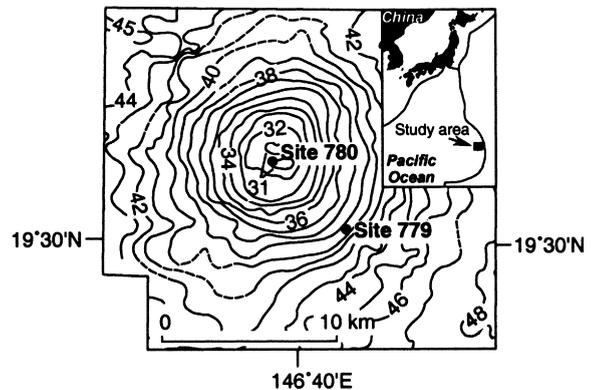

Fig. 1. Bathymetry of Conical Seamount showing locations of ODP Leg 125 Sites 779 and 780. Contours are in 100 m intervals. Inset shows location of Conical Seamount in the Pacific Ocean. Adapted from [16].

covered recent flows of clast-bearing serpentine muds and mineralized chimneys venting compositionally anomalous, cool fluids [17,23,25]. Subsequent study of several other seamounts (Pacman Seamount and South Chomorro Seamount) has also documented active fluid venting and 'cold-spring' biological communities [22,26]. Ocean Drilling Program (ODP) Leg 125 had as one of its primary goals the petrologic examination of Conical Seamount. Both the summit (Site 780) and flanks (Sites 778 and 779) were drilled, and both lithologic and pore fluid samples were collected [16].

Based on relict mineralogies and bulk composition, the protoliths of Conical Seamount serpentine mud flows are tectonized harzburgites and dunites, suggestive of an origin in the depleted upper mantle [16]. Hydration produced a secondary mineralogy dominated by serpentine. Both the unconsolidated serpentine and serpentinized ultramafic clasts from these cores are dominated by chrysotile ± lizardite and antigorite [16,27–29]. Chemically, the serpentinites show elevated B and Li concentrations, but have K, Sr and Ba abundances that are indistinguishable from upper mantle rocks [18,30]. Pore fluid samples from Site 780 at the Conical Seamount summit are compositionally unique, with unusually high pH (up to 12.6), low chlorinity (almost half that of seawater) and elevated abundances of B, Rb and K (up to

10, 5.6 and 1.5 times greater than seawater, respectively) [17]. The samples are also characterized by enrichment in CH_4 and organic acids relative to nearby forearc sediments [16,31] and $^{87}Sr/^{86}Sr$ ratios well below that of seawater [32], all suggestive of a subducted fluid source.

Table 1
B abundance and isotope data for Conical Seamount samples

Sample identification[a]	Depth (mbsf)	$\delta^{11}B$	2σ (‰)	B (ppm)
Serpentine matrix:				
125-779A-				
05R-3, 054–056	32.75	20.6	0.3	25.6
13R-1, 138–140	107.45	10.8	0.5	6.6
18R-2, 087–089	157.38			9.7
28R-2, 112–114	227.60	16.4	0.3	12.7
32R-2, 000–010	265.95			20.6
36R-2, 132–134	305.85	11.3	0.3	16.6
125-779B-				
01R-1, 117–119	1.18			126
125-780C-				
02R-1, 002–004	5.53	19.8	0.2	33.4
04R-1, 024–026	23.74			28.2
05R-1, 037–039	33.37	14.2	0.2	25.3
duplicate		14.3	0.6	
07R-1, 014–017	52.24	14.2	0.3	23.3
12R-1, 006–008	100.26			26.1
13R-1, 053–055	107.03	12.9	0.3	23.5
15R-1, 027–029	125.77	13.1	0.7	31.2
duplicate		13.2	0.5	
16R-1, 033–035	135.33			26.0
18R-1, 129–131	155.29			35.2
18R-1, 138–140	155.38	15.2	0.6	30.9
125-780D-				
01X-1, 026–028	0.26	11.0	0.2	81.1
02X-1, 035–037	2.85			29.2
06X-2, 033–035	21.51	14.2	0.3	29.0
07X-5, 123–125				29.8
Serpentinized peridotite clasts:				
125-779A-				
04R-1, 027–030	20.40	25.3	0.3	57.5
05R-2, 062–072	30.82	21.8	0.3	43.3
08R-1, 090–093	59.43	5.4	0.3	20.4
15R-2, 022–023	126.63	14.8	0.3	23.2
16R-1, 019–023	135.73	10.8	0.3	12.7
18R-2, 113–114	157.54	10.4	0.3	21.6
22R-1, 041–043	170.53	14.9	0.4	6.8
26R-3, 103–104	210.54	14.7	0.3	15.5
33R-2, 082–083	276.33	11.9	0.7	17.6

[a]Sample identification is according to the following ODP convention: 125 (ODP Leg)-779 (Site) A (Hole)-05 (Core) R (drilling method, e.g. R for rotary and X for extended core barrel)-3 (Section), 054–056 cm (interval).

3. Methodology

Samples were selected from ODP cores from Conical Seamount (Site 779 on the flank, Holes A and B and Site 780 on the summit, Holes C and D) (Fig. 1), and include both unconsolidated serpentine matrix and highly serpentinized ultramafic clasts. Clast samples were cut from the interiors of relatively vein-free core segments, on the presumption that the interiors would be less likely to suffer late-stage exchanges with seawater or other fluids. Both sample types predominantly consist of chrysotile ± lizardite or antigorite [16,29,33]. All samples were washed with deionized water to remove absorbed B and salts from pore fluids [34].

B concentrations for samples of serpentine matrix were measured by isotope dilution mass spectrometry (IDMS) at the Department of Terrestrial Magnetism (DTM) (Washington, DC, USA) using the HF-mannitol method of digestion [35] and positive ion thermal ionization mass spectrometry of $Cs_2BO_2^+$ [36,37]. Concentrations for the clast samples were measured by direct-current plasma emission spectrometry (DCP) at the University of South Florida (Tampa, FL, USA) using the Na_2CO_3 flux method of digestion [3]. Uncertainties are less than ±1% for IDMS measurements and ±10% for DCP measurements. All B isotope measurements were prepared and analyzed using methods similar to the IDMS analyses at DTM. Separate preparations and analysis of serpentine samples give values within 0.2‰ of each other, however the internal precision of individual runs frequently exceeds this level.

4. Results and discussion

4.1. Constraining seawater interactions

B abundance and isotopic data for these samples are presented in Table 1 and Fig. 2. In Fig. 2, serpentine matrix and serpentinized clast B abundances and B isotope compositions (reported as $\delta^{11}B$) and pore fluid pH and chlorinity are plotted against depth. At both sites, B abundances and $\delta^{11}B$ values are generally highest near the seafloor
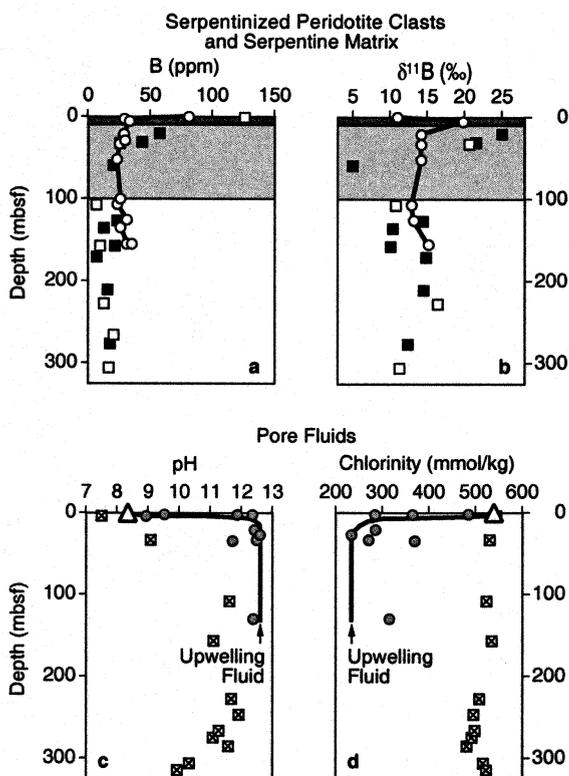
Fig. 2. Juxtaposition of depth profiles of B and δ^{11}B values for samples of unconsolidated serpentine matrix (open symbols) and serpentinized ultramafic clasts (solid symbols) along with pH and chlorinity values for samples of pore fluid (shaded circles or crossed squares) from ODP Sites 779 (squares) and 780 (circles) cores recovered from the flank and summit of Conical Seamount, respectively. Bold lines connect data points for matrix samples from ODP Site 780 to emphasize the depth profile in (a) and (b) and highlight the mixing relationship between seawater (triangles) and the upwelling fluid at the same site in (c) and (d). Shaded areas in (a) and (b) represent the depths at which samples are impacted by seawater at ODP Sites 779 (larger area) and 780 (smaller area). Note how the spike in δ^{11}B values corresponds to the changes in pore fluid pH and chlorinity. Pore fluid data are from [16].

and decrease with depth. This pattern of B enrichment is caused by the uptake of B from seawater by serpentine in the seamount. Alteration by seawater is a major concern with these materials, because seawater has a relatively high B content (4.5 ppm) and very high δ^{11}B of +40‰ [38]. At seafloor temperatures, B partitions preferentially into serpentine [38,39], resulting in higher B con-

centrations in serpentine re-equilibrating near the surface. Pore fluid compositions from summit Site 780 samples indicate near-surface seawater interactions down to ~ 10 m below seafloor (mbsf) [16,17]. In contrast, all the deeper samples have apparently been in chemical contact mainly with the unique alkaline, low chlorinity, B-rich pore fluids [16,17,40], which upwell through the seamount. At flank Site 779, pore fluids are compositionally a mixture of seawater and the upwelling fluid, but pH values generally exceed 11 below 100 mbsf [16,17].

As shown in Fig. 2, samples from Site 780 in contact with high pH, low chlorinity fluids show B abundances and B isotope compositions that reach nearly constant values $(\delta^{11}$B $\sim +14‰)$. Large abundance and isotope variations, however, occur in shallow samples at both sites, where chlorinity data indicates mixing between seawater and the upwelling fluid [17]. As B speciation in solution is strongly dependent on pH, essentially 100% of pore fluid B will be speciated as tetrahedral $B(OH)_4^-$ in the deeper fluids [8,38]. B isotope fractionations between solids and fluids are thought to relate to the preferential incorporation of ^{10}B-rich $B(OH)_4^-$ into silicate minerals. At present, the serpentine–water fractionation factor and its relationship between pH and temperature are not known. However, assuming that B is tetrahedrally coordinated in both the serpentine and the high pH fluids at Conical Seamount, then minimal isotopic fractionation should occur during exchanges between these pore fluids and the serpentine [38]. As a result, the B isotopic composition of the serpentine will represent the lower limit on the δ^{11}B (+13‰) of the pore fluids even if the effect of temperature on fractionation is significant. The magnitude of the temperature effect, however, is not expected to be large based on the high δ^{11}B of shallow matrix samples interacting with seawater-rich fluid mixtures at pH < 10 (e.g. 125-780C-02R-1, 2–4 cm; 5.5 mbsf; δ^{11}B = 19.8‰).

B isotopic variations also diminish with depth in samples from Site 779. The large abundance and isotopic variations in the upper 100 m are likely the result of mixing between B from seawater, the deep pore fluids and the clast mantle/

crustal protoliths at variable pH. Mixtures of the upwelling pore fluids (pH $\sim$ 12.6 [16]; $\sim$ 40 ppm B [40]; δ^{11}B $\sim$ +13‰) and seawater (pH = 8.2; 4.5 ppm B; δ^{11}B = +40‰ [38]) may span a range of B concentrations, δ^{11}B and pH. The δ^{11}B of serpentine exchanging with such mixed fluids will be affected not only by the B abundances and δ^{11}B of the fluids, but also by fluid pH. Seawater-rich fluid mixtures (90–95% seawater and 5–10% deep pore fluids) will have both low δ^{11}B and relatively low pH, and could thus produce serpentines with δ^{11}B as low as +5‰ during exchanges with ultramafic rocks. Such low δ^{11}B values are feasible because the relatively low pH of the pore fluids can generate significant serpentine–water isotopic fractionation related to differences in B coordination. B-rich serpentine formed at depth beneath Conical Seamount that interacts with seawater-rich fluids at shallower levels may undergo either increases or decreases in δ^{11}B, depending both on the pH and water–rock ratio of exchange. Site 779 clasts and shallow unconsolidated matrix samples with elevated δ^{11}B may record exchanges between serpentine formed at depth under high pH conditions with shallow fluids composed of 60–70% seawater. In contrast, the one low clast δ^{11}B value (125-779A-08R-1, 90–93 cm; 59.4 mbsf; δ^{11}B = 5.4‰) may represent an instance of shallow serpentine formation in the presence of a lower pH ($\sim$ 8.5) fluid containing 90–95% seawater.

At greater depths in Hole 779A, pore fluid pH exceeds 10, and both B abundances and B isotope data show less variability, with δ^{11}B values converging on the average value of the summit Site 780 samples at +14‰. While chlorinity data for the deeper portion of Site 779 indicates some seawater infiltration, the small range of variation in both the B abundances and δ^{11}B values suggest that late-stage B additions are limited in these samples. As a result, these samples primarily reflect equilibration with deep-sourced, B-rich fluids like the unconsolidated serpentine matrix of Site 780.

4.2. Source of B at Conical Seamount

Given the B contents and unusual B isotopic signatures of the Mariana serpentinites, the subducted slab is the only feasible fluid source. The possibility that the upwelling fluids at Conical Seamount are deep circulating seawater is inconsistent with inferences from pore fluid elemental abundances and δD and δ^{18}O data [17,18]. The hydrogen and oxygen isotopic compositions of serpentine from Conical Seamount are consistent with additions of fluids produced by the dehydration and/or breakdown of hydrous minerals at depth [18,41]. Calculations made using serpentine δD and δ^{18}O data to estimate the isotopic composition of a serpentinizing fluid at 150–200°C yield fluid δD values that are significantly lower than seawater and δ^{18}O values that are higher than both seawater and unaltered mantle values [18]. High pore fluid B concentrations are also inconsistent with seawater circulating at low temperature through forearc crust, as B partitioning experiments indicate $\sim$ 100% uptake of B by basalt at temperatures less than 150°C [42]. The possibility that seawater has overprinted a deeper sourced δ^{11}B signature in the serpentinite prior to emplacement of the clasts and matrix is also unlikely because of the high concentration of B in the upwelling fluid relative to seawater.

If subducted material is the source of the B in the upwelling fluids and serpentinites at Conical Seamount, then the downgoing Pacific slab must be releasing B beneath the forearc that is richer in [11]B than bulk estimates of either marine sediments or AOC, which are the primary B reservoirs of the downgoing plate [8,38,43–45]. The 'desorbable' B component in marine sediments (as defined by [8,34]) has a δ^{11}B of +14 to +16‰, comparable to that of the serpentinites. This 'desorbable' component can be liberated into pore fluids by sediment compaction in accretionary prisms. To generate the δ^{11}B of the Conical serpentinites would require that the B in the upwelling fluids be $\sim$ 100% 'desorbable' all of which would come from the subducted slab because the Marianas is a non-accretionary margin. However, the upwelling fluids from Site 780 show chemical and isotopic signatures (e.g. chlorinity, B, Rb, K, δD and δ^{18}O) consistent with release by hydrous mineral reactions at depth, processes that should liberate structurally bound B from the slab. Struc-

turally bound B in subducting sediments is both higher in abundance ($\sim$85% of the B inventory in subducting sediments) and isotopically lighter ($\delta^{11}B \sim -10$ to $-3‰$) than 'desorbable' B [34,44,46]. Any significant addition of structurally bound B to the serpentinizing fluids should serve to reduce the $\delta^{11}B$ of the resultant serpentinites to values lower than those we observe.

If, however, some degree of B isotopic mass fractionation occurs during the release of structurally bound B from the slab, during low temperature ($<300°C$) mineral fluid reactions, the $\delta^{11}B$ values observed in Conical serpentinites can be generated. All of the B isotopic fractionation reactions that have been studied involve the generation of ^{11}B-enriched fluid phases [46–48]. The degree of ^{11}B enrichment in the fluids is smaller

at higher temperatures, but even at temperatures as high as 600°C shifts of 3–4‰ have been documented for tourmaline [48]. In order to produce the $\delta^{11}B$ signatures of the Conical Seamount serpentinites, the evolved slab-derived fluid phase would need to have $\delta^{11}B$ values $\sim$9–16‰ higher than the slab (assuming an average $\delta^{11}B$ of +4‰ for AOC [45] and $-3‰$ for bulk marine sediments based on Nankai Trough sediments [49]).

4.3. Significance for the B budget of subduction zones

The loss of ^{11}B-enriched fluids from the slab in forearc regions may help clarify models of slab B inputs at volcanic arcs. Fig. 3 plots B isotopes (as $\delta^{11}B$) versus slab depth for our serpentinite data,
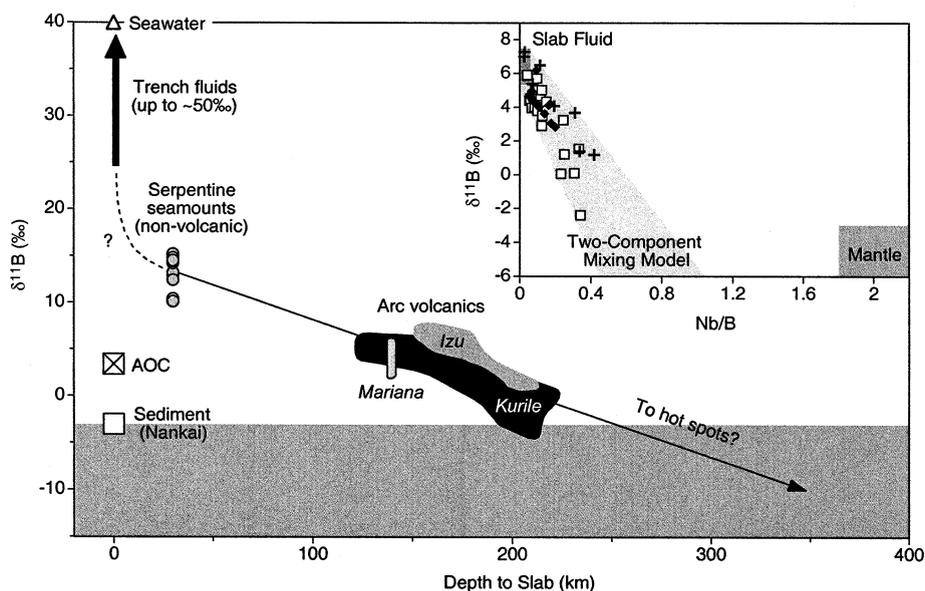

Fig. 3. Depth to the subducted slab plotted against $\delta^{11}B$ of Conical Seamount serpentinites, lavas from the Mariana [6], Izu [2] and Kurile [5] arcs, seawater [38], Nankai Trough pore fluids (ODP Site 808) [49] (bold arrow), average AOC [45] and average Nankai Trough sediment (ODP Site 808) [49]. Depths to the Wadati–Benioff zone [2,5] are used as depths to the subducting slab for the Izu and Kurile arc volcanics. Mariana arc data are assigned a slab depth of 140 km based on [59]. Shaded area at the bottom of plot indicates the range of estimates for mantle $\delta^{11}B$ values [38,50–53]. Solid line highlights the relationship between slab $\delta^{11}B$ and slab depths. The trend is consistent with the release of fluids enriched in ^{11}B relative to the slab at depths extending to greater than 200 km. Inset contains a plot of Nb/B against $\delta^{11}B$ of Izu [2] (crosses), North Kurile (open squares) and South Kurile [5] (closed diamonds) arc lavas. Shaded box indicates the inferred range of $\delta^{11}B$ values for a slab fluid 'end-member' [2,5,6]. If the slab is continuously losing B enriched in ^{11}B, then such end-members must be location specific. However, in a two-component mixing model, these location specific end-members are unlikely because they would require extensive mantle mixing.

as well as published data for volcanic rocks from the Kurile, Izu and Mariana arcs [2,5,6], all in the western Pacific. $B-^{10}Be$ and B isotope relationships in these arcs point to the involvement of a B-enriched, hydrous fluid from the slab [3,7]. B isotope–Nb/B correlations in lavas from these arcs were initially interpreted as simple mixtures of mantle-derived B and a fluid component with a specific B isotopic composition ($\delta^{11}B = +5$ to $+8\%o$ [2,5,6]; see inset Fig. 3). The high $\delta^{11}B$ of the fluid component constrained the slab source of fluid B as AOC, given that marine sediments are too depleted in ^{11}B to be a reasonable source. Central to these models is the presumption that little or no significant fractionation of the B isotopes occurs at depth in subduction zones.

These early mixing models for B have become problematic with the publication of more extensive B isotope data sets. The mean $\delta^{11}B$ AOC at $\sim +4\%o$ is slightly poorer in ^{11}B than the hypothesized fluid end-members for either the Izu or Kurile suites. More importantly, the growing body of data on MORBs and intraplate volcanic rocks places mantle $\delta^{11}B$ between $-3\%o$ and $-14\%o$ [38,50–53] at markedly low B abundances, (i.e. Nb/B ratios of MORBs and OIBs are ≥ 2.0 [54] and references herein) as compared to typical arc values for Nb/B of 0.05 to 0.4 [2,5,6] (Fig. 3, inset). The low $\delta^{11}B$ 'end-members' of the Pacific cross-arc data arrays have Nb/B ratios considerably less than 1.0 at $\delta^{11}B$ values consistent with MORB or OIB mantle source regions. To modify a MORB mantle source to such a low Nb/B ratio either would require dramatic depletions in Nb or marked enrichments in B. While arc lavas are distinctively low in Nb, this effect is usually attributed to retention of Nb in residual slab titanite phases and not to mantle depletions [55]. Extreme B enrichment is also unlikely because $^{10}Be/^9Be$–B/Be correlations in arcs demonstrate that mantle reservoirs globally contain negligible ^{10}Be or B [7]. Barring such previously unrecognized effects, the current data for B isotopes in arcs and mantle-derived rocks cannot be explained by fluid–mantle mixing alone.

The mean $\delta^{11}B$ of the seamount serpentinites at $+14\%o$ extends the trend formed by the arc data to shallower depths. If the Conical Seamount fluids represent B releases from the slab, then shallow devolatilization processes are removing from the subducting plate a B component that is isotopically heavier than either the slab as a whole or any slab component. These data necessitate the occurrence of some sort of B isotopic fractionation during fluid releases, with ^{11}B being preferentially removed by the liberated fluids.

With the apparent extension of the Pacific arc data trend into the forearc, we propose an explanation in which the pattern of $\delta^{11}B$ variations with depth of subduction reflects the effect of continuous, though decreasing, inputs of B from a slab that is evolving isotopically because of the preferential loss of ^{11}B. Declining $^{207}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ ratios across the Izu and Kurile arcs, respectively [5,56], and changing Sr, Pb and Nd isotope ratios across the Sunda arc [57] all point to diminishing slab additions of these elements in lavas erupted over deeper segments of slabs, as do cross-arc declines in B concentrations, B/Be and Nb/B [2,4,5,58]. On plots of $\delta^{11}B$ versus Nb/B, cross-arc data arrays approach linearity because of the complementary effects of slab fluid–mantle mixing, and the progressive evolution of ^{11}B-enriched fluids from a slab with progressively lower $\delta^{11}B$. At each depth, the slab fluid input with a specific B content and $\delta^{11}B$ value triggers mantle melting and B from the slab dominates the $\delta^{11}B$ value of the erupted lava. For arc lavas erupted at the volcanic front, more than 90% of the B is slab-derived [11,57]. As slab depth increases, the progressive removal of fluids serves to drive the slab to lower $\delta^{11}B$ values and lower B abundances. Only when the magnitude of slab fluid inputs of B become negligible, and the $\delta^{11}B$ of slab B becomes low (as it does in the rearmost portions of arcs) does the $\delta^{11}B$ contribution of the mantle wedge become significant.

An interesting implication of this sort of model is that deeply subducted slabs may develop low B contents depleted in ^{11}B. Intraplate lavas show absolute B depletions as compared to MORBs [54], and also have variable low $\delta^{11}B$ [51,52]. B isotopic variation in intraplate lavas may thus be a valuable tool for identifying the geochemical 'fingerprints' of deeply subducted slabs.

5. Conclusions

The main findings of our work on the serpentinites of Conical Seamount are (1) forearc releases of subducted B by way of Conical Seamount are enriched in [11]B relative to the subducted slab; (2) both the unconsolidated serpentine matrix and serpentinized ultramafic clasts have δ^{11}B values that converge on +13‰; (3) the upwelling slab fluid must be enriched in [11]B and the high pH of the pore fluids should minimize fluid-mineral isotopic fractionation such that the δ^{11}B of the upwelling slab fluid is inferred to be +13‰; (4) shallow samples are impacted by seawater, but can be identified by variable δ^{11}B values, elevated B abundances and pore fluid data.

The trend of decreasing δ^{11}B with slab depth described for arc magmas of the western Pacific extends to shallow depths (~ 25 km) when the inferred δ^{11}B of the slab fluid (+13‰) at Conical Seamount is considered. This apparent extension of the trend into the forearc cannot be explained by the two-component mixing model used to explain the arc data [2,5,6]. Instead, some degree of B isotopic fractionation is required and the trend reflects the effect of continuous, though decreasing, inputs of B from a slab that is evolving isotopically because of the preferential loss of [11]B. As a result, the slab is losing [11]B-enriched fluids from the shallowest levels to depths as great as 200 km.

Acknowledgements

References

[1] M.R. Palmer, Boron-isotope systematics of Halmahera arc (Indonesia) lavas: Evidence for involvement of the subducted slab, Geology 19 (1991) 215–217.

[2] T. Ishikawa, E. Nakamura, Origin of the slab component in arc lavas from across-arc variation of B and Pb isotopes, Nature 370 (1994) 205–208.

[3] J.G. Ryan, C.H. Langmuir, The systematics of boron abundances in young volcanic rocks, Geochim. Cosmochim. Acta 57 (1993) 1489–1498.

[4] J.G. Ryan, J. Morris, F. Tera, W.P. Leeman, A. Tsvetkov, Cross-arc geochemical variations in the Kurile Arc as a function of slab depth, Science 270 (1995) 625–627.

[5] T. Ishikawa, F. Tera, Source, composition and distribution of the fluid in the Kurile mantle wedge; constraints from across-arc variations of B/Nb and B isotopes, Earth Planet. Sci. Lett. 152 (1997) 123–138.

[6] T. Ishikawa, F. Tera, Two isotopically distinct fluid components involved in the Mariana arc: evidence from Nb/B ratios and B, Sr, Nd, and Pb isotope systematics, Geology 27 (1999) 83–86.

[7] J.D. Morris, W.P. Leeman, F. Tera, The subducted component in island arc lavas: constraints from Be isotopes and B–Be systematics, Nature 344 (1990) 31–36.

[8] A.J. Spivack, Boron Isotope Geochemistry, Ph.D. Dissertation, Woods Hole Oceanographic Institute, MIT Press, Cambridge, MA, 1986.

[9] J.G. Ryan, The Systematics of Lithium, Beryllium and Boron in Young Volcanic Rocks, Ph.D. Dissertation, Columbia University, New York, 1989.

[10] C.-F. You, A.J. Spivack, J.H. Smith, J.M. Gieskes, Mobilization of boron in convergent margins: implications for the boron geochemical cycle, Geology 21 (1993) 207–210.

[11] J. Ryan, J. Morris, G.E. Bebout, B. Leeman, Describing chemical fluxes in subduction zones; insights from 'depth-profiling' studies of arc and forearc rocks, in: G.E. Bebout, D.W. Scholl, S.H. Kirby, J.P. Platt (Eds.), Subduction Top to Bottom, Geophysical Monograph Series 96, Am. Geophys. Union, Washington, DC, 1996, pp. 263–268.

[12] H.J. Smith, W.P. Leeman, J. Davidson, A.J. Spivack, The B isotopic composition of arc lavas from Martinique, Lesser Antilles, Earth Planet. Sci. Lett. 146 (1997) 303–314.

[13] P. Fryer, E.L. Ambos, D.M. Hussong, Origin and emplacement of Mariana forearc seamounts, Geology 13 (1985) 774–777.

[14] D.M. Hussong, P. Fryer, Fore-arc tectonics in the Northern Mariana Arc, in: N. Nasu, K. Kobayashi, I. Kushiro, H. Kagami (Eds.), Formation of Active Ocean Margins, Terra Sci. Publ., Tokyo, 1985, pp. 273–290.

[15] P. Fryer, G.J. Fryer, Origins of nonvolcanic seamounts in a forearc environment, in: B.H. Keating, P. Fryer, R. Batiza, G.W. Boelert (Eds.), Seamounts, Islands, and Atolls, Geophysical Monograph Series 43, Am. Geophys. Union, Washington, DC, 1987, pp. 61–69.

[16] P. Fryer, J.A. Pearce, L.B. Stokking et al., Proc. Ocean Drill. Prog., Initial Reports, Ocean Drill. Prog., College Station, TX, 1990.

[17] M.J. Mottl, Pore waters from serpentine seamounts in the Mariana and Izu–Bonin Forearcs, Leg 125: evidence for volatiles from the subducting slab, Proc. ODP Sci. Results 125 (1992) 373–385.

[18] L.D. Benton, Origin and Evolution of Serpentine Seamount Fluids, Mariana and Izu–Bonin Forearcs: Implications for the Recycling of Subducted Material, Ph.D. Dissertation, University of Tulsa, 1997.

[19] P. Fryer, C. Wheat, M. Mottl, Mariana blueschist mud volcanism; implications for conditions within the subduction zone, Geology 27 (1999) 103–106.

[20] D.M. Hussong, S. Uyeda, Tectonic processes and the history of the Mariana Arc: a synthesis of the results of the Deep Sea Drilling Project Leg 60, Init. Rep. DSDP 60 (1981) 909–929.

[21] T. Ishii, Dredged samples form the Ogasawara fore-arc seamount or 'Ogasawara paleoland'-'fore-arc ophiolite', in: N. Nasu, K. Kobayashi, I. Kushiro, H. Kagami (Eds.), Formation of Active Ocean Margins, Terra Sci. Publ., Tokyo, 1985, pp. 307–342.

[22] P. Fryer, C.G. Wheat, M.J. Mottl, Mariana blueschist mud volcanism; implications for conditions within the subduction zone, Geology 27 (1999) 103–106.

[23] P. Fryer, K.L. Saboda, L.B. Johnson, M.E. Mackay, G.F. Moore, P. Stoffers, Conical Seamount: SeaMARK II, *Alvin* submersible, and seismic reflection studies, Proc. ODP Init. Rep. 125 (1990) 69–80.

[24] R. Sakai, M. Kusakabe, M. Noto, T. Ishii, Origin of waters responsible for serpentinization of the Izu–Ogasawara–Mariana forearc seamounts in view of hydrogen and oxygen isotope ratios, Earth Planet. Sci. Lett. 100 (1990) 291–303.

[25] J.A. Haggerty, Evidence from fluid seeps atop serpentine seamounts in the Mariana forearc: clues for emplacement of the seamounts and their relationship to forearc tectonics, Mar. Geol. 102 (1991) 293–309.

[26] P. Fryer, M. Mottl, L. Johnson, J. Haggerty, S. Phipps, H. Maekawa, Serpentine bodies in the forearcs of western Pacific convergent margins: origin and associated fluids, in: B. Taylor, J. Natland (Eds.), Active Margins and Marginal Basins of the Western Pacific, Geophysical Monograph Series, vol. 88, Am. Geophys. Union, Washington, DC, 1995, pp. 259–279.

[27] P. Fryer, M.J. Mottl, Lithology, mineralogy, and origin of serpentine muds recovered from Conical and Torishima forearc seamounts: results of Leg 125 drilling, Proc. ODP Sci. Results 125 (1992) 343–362.

[28] Y. Lagabrielle, A.-M. Karpoff, J. Cotten, Mineralogical and geochemical analyses of sedimentary serpentines from Conical Seamount (Hole 778A): implications for the evolution of serpentine seamounts, Proc. ODP Sci. Results 125 (1992) 325–342.

[29] K.L. Saboda, P. Fryer, H. Maekawa, Metamorphism of ultramafic clasts from Conical Seamount: Sites 778, 779, and 780, Proc. ODP Sci. Results 125 (1992) 431–443.

[30] P.D. Mattie, J.D. Ryan, Boron and alkaline element systematics in serpentinites from Holes 779A, 780C, and 784A, ODP Leg 125 describing fluid-mediated slab additions, EOS 75 (1994) 352.

[31] J.A. Haggerty, J.B. Fisher, Short-chain organic acids in interstitial waters from the Mariana and Bonin forearc serpentines, Proc. ODP Sci. Results 125 (1992) 387–395.

[32] J.A. Haggerty, S. Chaudhuri, Strontium isotopic composition of the interstitial waters from Leg 125: Mariana and Bonin forearcs, Proc. ODP Sci. Results 125 (1992) 397–400.

[33] D. Heling, A. Schwarz, Iowaite in serpentinite muds at Sites 778, 779, 780 and 784: a possible cause for the low chlorinity of pore waters, Proc. ODP Sci. Results 125 (1992) 313–323.

[34] A.J. Spivack, M.R. Palmer, J.M. Edmond, The sedimentary cycle of the boron isotopes, Geochim. Cosmochim. Acta 51 (1987) 1939–1949.

[35] E. Nakamura, T. Ishikawa, J.-L. Birck, C.J. Allegre, Precise boron isotopic analysis of natural rock samples using a boron–mannitol complex, Chem. Geol. 94 (1992) 193–204.

[36] A.J. Spivack, J.M. Edmond, Determination of boron isotope ratios by thermal ionization mass spectrometry of the dicesium metaborate cation, Anal. Chem. 58 (1986) 31–35.

[37] Y.-F. Xiao, E.S. Beary, J.D. Fassett, An improved method for the high-precision isotopic measurement of boron by thermal ionization mass spectrometry, Int. J. Mass Spectr. Ion Proc. 85 (1988) 203–213.

[38] A.J. Spivack, J.M. Edmond, Boron isotope exchange between seawater and the oceanic crust, Geochim. Cosmochim. Acta 51 (1987) 1033–1043.

[39] E. Bonatti, J.R. Lawrence, N. Morandi, Serpentinization of oceanic peridotites: temperature dependence of mineralogy and boron content, Earth Planet. Sci. Lett. 70 (1984) 88–94.

[40] M.J. Mottl, J.C. Alt, Data report: minor and trace element and sulfur isotopic composition of pore waters from Sites 778 through 786, Proc. ODP Sci. Results 125 (1992) 683–687.

[41] M. Kastner, H. Elderfield, J.B. Martin, Fluids in convergent margins: what do we know about their composition, origin, role in diagenesis and importance for iceanic chemical fluxes?, Philos. Trans. R. Soc. Lond. A 335 (1991) 243–259.

[42] W.E. Seyfried Jr., D.R. Janecky, M.J. Mottl, Alteration of the oceanic crust: implications for geochemical cycles of lithium and boron, Geochim. Cosmochim. Acta 48 (1984) 557–569.

[43] T. Ishikawa, E. Nakamura, Boron isotope geochemistry

of the oceanic crust from DSDP/ODP Hole 504B, Geochim. Cosmochim. Acta 56 (1992) 1633–1639.

[44] T. Ishikawa, E. Nakamura, Boron isotope systematics of marine sediments, Earth Planet. Sci. Lett. 117 (1993) 567–580.

[45] H.J. Smith, A.J. Spivack, S.R. Hart, The boron isotopic composition of altered oceanic crust, Chem. Geol. 126 (1995) 119–135.

[46] C.-F. You, A.J. Spivack, J.M. Gieskes, R. Rosenbauer, J.R. Bischoff, Experimental study of boron geochemistry: implications for fluid processes in subduction zones, Geochim. Cosmochim. Acta 59 (1995) 2435–2442.

[47] M.R. Palmer, A.J. Spivack, J.M. Edmond, Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay, Geochim. Cosmochim. Acta 51 (1987) 2319–2323.

[48] M.R. Palmer, D. London, G.B.V. Morgan, H.A. Babb, Experimental determination of fractionation of $^{11}B/^{10}B$ between tourmaline and aqueous vapor; a temperature- and pressure-dependent isotopic system, Chem. Geol. 101 (1992) 123–129.

[49] C.-F. You, L.H. Chan, A.J. Spivack, J.M. Gieskes, Lithium, boron, and their isotopes in sediments and pore waters of Ocean Drilling Program Site 808, Nankai Trough: implications for fluid expulsion in accretionary prisms, Geology 23 (1995) 37–40.

[50] M. Chaussidon, A. Jambon, Boron content and isotopic composition of oceanic basalts; geochemical and cosmochemical implications, Earth Planet. Sci. Lett. 121 (1994) 277–291.

[51] M. Chaussidon, B. Marty, Primitive boron isotope composition of the mantle, Science 269 (1995) 383–386.

[52] A.A. Gurenko, M. Chaussidon, Boron concentrations and isotopic composition of the Icelandic mantle; evidence from glass inclusions in olivine, Chem. Geol. 135 (1997) 21–34.

[53] M. Roy-Barman, G.J. Wasserburg, D.A. Papanastassiou, M. Chaussidon, Osmium isotopic compositions and Re–Os concentrations in sulfide globules from basaltic glasses, Earth Planet. Sci. Lett. 154 (1998) 331–347.

[54] J.G. Ryan, W.P. Leeman, J.D. Morris, C.H. Langmuir, The boron systematics of intraplate lavas: implications for crust and mantle evolution, Geochim. Cosmocim. Acta 60 (1996) 415–422.

[55] J.M. Brenan, H.F. Shaw, D.L. Phinney, F.J. Ryerson, Rutile-aqueous fluid partitioning of Nb, Ta, Hf, Zr, U and Th; implications for high field strength element depletions in island-arc basalts, Earth Planet. Sci. Lett. 128 (1994) 327–339.

[56] A.A. Zhuravlev, A.Z. Tsvetkov, N.G. Gladkov, I.V. Chernyshev, $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios in recent magmatic rocks of the Kurile island arc, Chem. Geol. 66 (1987) 227–243.

[57] C.M.H. Edwards, J.D. Morris, M.F. Thirlwall, Separating mantle from slab signatures in arc lavas using B/Be and radiogenic isotope systematics, Nature 362 (1993) 530–533.

[58] P.D. Noll Jr., H.E. Newsom, W.P. Leeman, J.G. Ryan, The role of hydrothermal fluids in the production of subduction zone magmas; evidence from siderophile and chalcophile trace elements and boron, Geochim. Cosmochim. Acta 60 (1996) 587–611.

[59] B.L. Isacks, M. Barazangi, Geometry of Benioff zones; lateral segmentation and downwards bending of the subducted lithosphere, Maurice Ewing Ser. 1 (1977) 99–114.