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# Boron isotopic composition of subduction-zone metamorphic rocks

Simon M. Peacock<sup>a,\*</sup>, Richard L. Hervig<sup>a,b</sup>

<sup>a</sup> Department of Geology, Arizona State University, Tempe, AZ 85287-1404, USA

<sup>b</sup> Center for Solid State Science, Arizona State University, Tempe, AZ 85287-1704, USA

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## Abstract

Many arc lavas contain material derived from subducted oceanic crust and sediments, but it remains unresolved whether this distinctive geochemical signature is transferred from the subducting slab by aqueous fluids, silicate melts, or both. Boron isotopic measurements have the potential to distinguish between slab transfer mechanisms because  $^{11}\text{B}$  fractionates preferentially into aqueous fluids whereas little fractionation may occur during partial melting. Previous studies have shown that  $\delta^{11}\text{B}$  values of island arc lavas ( $-6$  to  $+7$ ) overlap the range of  $\delta^{11}\text{B}$  values for altered oceanic crust ( $-5$  to  $+25$ ) and pelagic sediments and turbidites ( $-7$  to  $+11$ ). Secondary ion mass spectrometry (SIMS) analyses of minerals in subduction-zone metamorphic rocks yield  $\delta^{11}\text{B} = -11$  to  $-3$  suggesting that slab dehydration reactions significantly lower the  $\delta^{11}\text{B}$  values of subducted oceanic crust and sediments. In order to explain the higher  $\delta^{11}\text{B}$  values reported for arc lavas as compared to subduction-zone metamorphic rocks, the B-bearing component derived from the metamorphosed slab must be enriched in  $^{11}\text{B}$  relative to the slab, favoring an aqueous fluid as the slab transfer mechanism. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Boron isotopes; Subduction; Metamorphism

## 1. Introduction

Geochemical, isotopic, and petrologic data support the view that most arc magmas are generated by partial melting of the mantle wedge induced by the infiltration of  $\text{H}_2\text{O}$  derived from the subducting slab (e.g., Gill, 1981; Hawkesworth et al., 1993; Davidson, 1996). This view is consistent with heat-transfer calculations which indicate the subducting oceanic

crust lies at subsolidus conditions ( $500$ – $700^\circ\text{C}$ ) at  $100$ – $150$  km depth (Peacock, 1996). Plank and Langmuir (1993) and Plank and Johnson (1997) have proposed that the efficient recycling of Be and Th from subducted sediment into arc magmas suggests the slab component includes a silicate melt derived from subducted sediments. If correct, the temperature of the slab–mantle interface at  $100$ – $150$  km depth must exceed  $\sim 650^\circ\text{C}$  — the wet solidus of pelagic sediment (Nichols et al., 1996). Other researchers have proposed that partial melting of the subducting oceanic crust is an important process in arc magma genesis (e.g., Marsh, 1979; Myers and

\* Corresponding author. Tel.: +1-480-965-1733; fax: +1-480-965-8102; E-mail: peacock@asu.edu

Johnston, 1996), particularly where anomalously young, hot lithosphere is being subducted (Drummond and Defant, 1990).

Compared to mid-ocean ridge basalts and oceanic island basalts, arc lavas are enriched in characteristic trace elements, including large-ion lithophile elements, B, and  $^{10}\text{Be}$ , which appear to be derived from the subducting oceanic crust and sediments (e.g., Gill, 1981; Pearce, 1982; Tera et al., 1986; Morris et al., 1990; Hawkesworth et al., 1993). Boron is a particularly good indicator of mass transfer in subduction zones because arc lavas contain 2–80 ppm B whereas depleted mantle contains  $\leq 0.1$  ppm B (Leeman and Sisson, 1996). A 5–10% partial melt of depleted upper mantle will contain  $\leq 2$  ppm B assuming a bulk-rock/melt B partition coefficient of 0.004 to 0.009 (Ryan and Langmuir, 1993). Thus, an additional boron source is required to explain the relatively high B concentrations in arc lavas. Published chemical analyses of marine sediments and altered oceanic crust show a wide range of boron concentrations from  $\sim 1$  to  $> 100$  ppm (e.g., Ishikawa and Nakamura, 1993; Smith et al., 1995; Leeman and Sisson, 1996) which suggests that most of the boron in arc magmas is derived from subducted marine sediments and oceanic crust. In many arcs, the concentration of boron relative to incompatible elements decreases with increasing distance from the trench which is interpreted to reflect a decrease in the slab component with increasing distance from the trench (Morris et al., 1990; Ryan et al., 1995).

How the distinct geochemical signature of the subducting slab is transferred into the mantle wedge remains a critical question. Possible transfer mechanisms include (i) aqueous fluids derived from slab dehydration reactions, (ii) silicate melts derived from partial melting reactions, and (iii) a combination of the two processes (e.g., sediments undergo partial melting whereas the basaltic oceanic crust dehydrates).

## 2. Boron isotopes

The isotopic ratio of boron can help define the mechanism of mass transfer between the slab and the overlying mantle wedge. Boron has two stable isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , with a terrestrial abundance ratio

of approximately 1:4. Following convention, we report isotopic analyses as per mil variations in the boron isotopic composition of a sample relative to the boron isotopic standard (NIST 951 boric acid; Cantanzaro et al., 1970) using standard delta notation:

$$\delta^{11}\text{B} = \left\{ \left[ \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} \right] - 1 \right\} \times 1000 \quad (1)$$

The mass difference between  $^{11}\text{B}$  and  $^{10}\text{B}$  (about 10%) is approximately the same as between  $^{18}\text{O}$  and  $^{16}\text{O}$ , but terrestrial samples exhibit a very large range of  $\delta^{11}\text{B}$  values ( $-30$  to  $+50$ ) (Palmer and Swihart, 1996). This large range in boron isotopic compositions likely reflects the tendency of the lighter boron isotope,  $^{10}\text{B}$ , to occupy tetrahedrally coordinated crystallographic sites whereas  $^{11}\text{B}$  tends to occupy trigonal sites (Kakihana et al., 1977; Oi et al., 1989; Palmer and Swihart, 1996). In most minerals and probably silicate melts, boron occupies tetrahedral sites whereas boron in aqueous fluids is in trigonal coordination (note that at high pH and  $T < \sim 50^\circ\text{C}$ , boron can be in tetrahedral coordination in solution). Experimental studies show that boron isotopic fractionation between water and clays (Palmer et al., 1987), water and borax (Oi et al., 1991), and water and carbonates (Hemming et al., 1995) are similar to, or larger than, the theoretical fractionation predicted by Oi et al. (1989) (Fig. 1). Recently, Hervig et al. (1997) showed that this relation also holds for boron isotopic fractionation between rhyolite melt and hydrous vapor at 650 and 750°C (Hervig et al., 1997). In each of these studies,  $^{11}\text{B}$  partitions preferentially into liquid water or water vapor relative to minerals and silicate melt.

There are some complications in this apparently simple relationship. The fractionation of B isotopes between borate solutions and borax is approximately one-half that predicted by Oi et al. (1989) (Fig. 1). However, in borax 50% of the boron is in trigonal coordination. The fractionation between the tetrahedral boron sites in borax and trigonally coordinated boron in solution would presumably be closer to the theoretical line. The study of rhyolite–water vapor fractionation (Hervig et al., 1997) is also complicated in that the B coordination in the melt is not

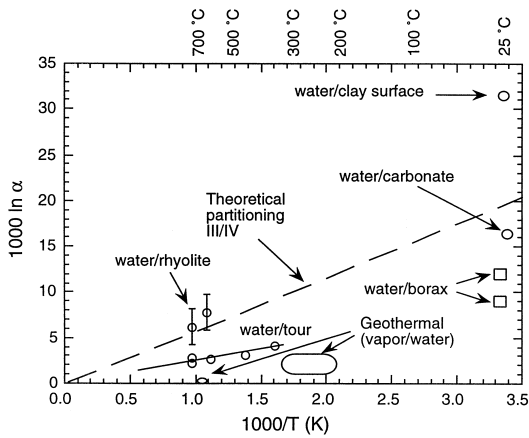


Fig. 1.  $1000 \ln \alpha$  vs. reciprocal  $T$  (K) showing different published boron isotope fractionations between water (liquid or vapor) and solid phases or between water vapor and liquid water ( $\alpha = {}^{11}\text{B}/{}^{10}\text{B}_{\text{water}}/{}^{11}\text{B}/{}^{10}\text{B}_{\text{other}}$ ). Vapor/tourmaline, Palmer et al. (1992); water/carbonate, Hemming et al. (1995); vapor/rhyolite melt, Hervig et al. (1997); vapor/borax, Oi et al. (1991); vapor/water, Spivack et al. (1990) and Leeman et al. (1992); and vapor/clay mineral surface, Palmer et al. (1987); theoretical fractionation of boron between trigonal and tetrahedral sites, Oi et al. (1989).

known. Nuclear magnetic resonance (NMR) spectroscopy of nominally dry silicate glasses in a simple system ( $\text{K}_2\text{O}-\text{SiO}_2-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ ) indicates that B is dominantly tetrahedral (Gan et al., 1994), whereas a preliminary NMR study of synthetic, B-rich hydrous rhyolitic glasses showed mostly trigonal boron (Morgan et al., 1990).

Regardless of the cause, the large boron isotopic fractionations observed between aqueous fluids and melts and between aqueous fluids and minerals suggests that this system can provide a powerful chemical tool for discriminating between different mechanisms for transferring boron from the subducting slab into arc magmas. If boron is transferred to the mantle wedge by aqueous fluids derived from slab dehydration reactions, then the aqueous fluids will be enriched in  ${}^{11}\text{B}$ . Conversely, if boron is transferred to the mantle wedge by silicate melts derived from partial melting of the slab, then we would expect the  $\delta^{11}\text{B}$  values of the slab and the partial melt to be similar.

Over the past 10–15 years, improvements in analytical techniques (e.g., Spivack and Edmond, 1986)

have dramatically increased our understanding of the variation of boron isotopic ratios in natural samples (see reviews by Barth, 1993; Leeman and Sisson, 1996; Palmer and Swihart, 1996). Previous studies have shown that  $\delta^{11}\text{B}$  values of island arc lavas broadly overlap the range of  $\delta^{11}\text{B}$  values for pelagic sediments, trench turbidites, and altered oceanic crust (Fig. 2). The  $\delta^{11}\text{B}$  values for modern pelagic sedi-

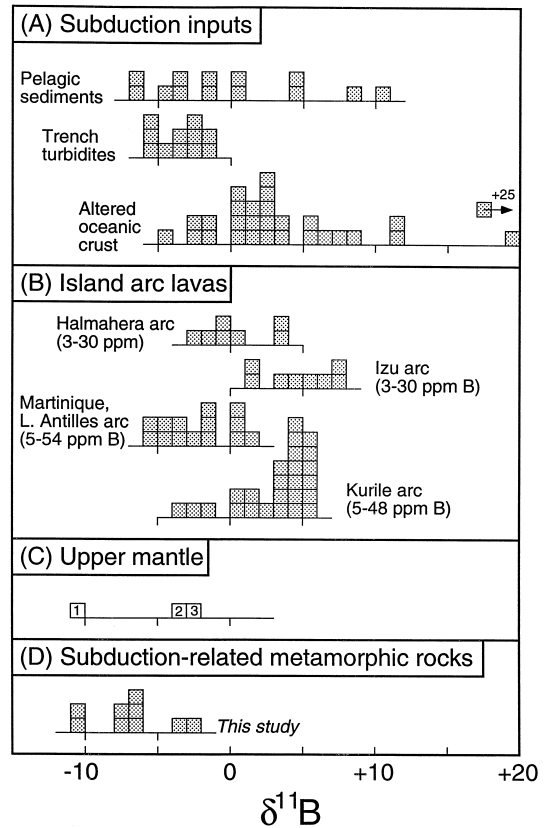


Fig. 2. Histogram showing  $\delta^{11}\text{B}$  values of selected rocks and minerals relevant to subduction zones. (A) Subduction inputs: modern pelagic sediments, typical  $2\sigma$  analytical uncertainty =  $\pm 0.1\%$  (Ishikawa and Nakamura, 1993); trench turbidites, Nankai Trough,  $2\sigma = \pm 0.4\%$  (You et al., 1995); altered oceanic crust,  $2\sigma = \pm 0.4\%$  (Smith et al., 1995). (B) Island arc lavas: Halmahera arc,  $2\sigma = 0.35\%$  (Palmer, 1991); Izu arc (Ishikawa and Nakamura, 1994); Martinique, Lesser Antilles arc,  $2\sigma = 0.4\%$  (Smith et al., 1997); Kurile arc,  $2\sigma = 0.2\%$  (Ishikawa and Tera, 1997). (C) Estimates of upper mantle  $\delta^{11}\text{B}$  values: 1 — Chaussidon and Marty (1995); 2 — Spivack and Edmond (1987); 3 — Ishikawa and Nakamura (1994). (D) Subduction related metamorphic rocks,  $2\sigma = \pm 1-6\%$ , this study.

ments range from  $-7$  to  $+11$  (Ishikawa and Nakamura, 1993),  $\delta^{11}\text{B}$  values for trench turbidites range from  $-6$  to  $-1$  (You et al., 1995), and  $\delta^{11}\text{B}$  values for altered oceanic crust range from  $-5$  to  $+25$  (Smith et al., 1995). The  $\delta^{11}\text{B}$  values of island arc lavas ranges from  $-6$  to  $+7$ . Lavas from the Halmahera arc yield  $\delta^{11}\text{B} = -2$  to  $+4$  (Palmer, 1991), from the Izu arc yield  $\delta^{11}\text{B} = +1$  to  $+7$  (Ishikawa and Nakamura, 1994), from Martinique in the Lesser Antilles arc yield  $\delta^{11}\text{B} = -6$  to  $+2$  (Smith et al., 1997), and from the Kurile arc yield  $\delta^{11}\text{B} = -4$  to  $+6$  (Ishikawa and Tera, 1997). In the Izu and Kurile arcs,  $\delta^{11}\text{B}$  values decrease with increasing distance from the trench which has been interpreted as a result of decreasing B input from the subducting slab (Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997). Estimates of the  $\delta^{11}\text{B}$  value of the upper mantle (Fig. 2) range from  $-10$  for primitive upper mantle based on oceanic island basalts (Chaussidon and Marty, 1995) to  $-4$  to  $-2$  for depleted upper mantle (Spivack and Edmond, 1987; Ishikawa and Nakamura, 1994).

The similar  $\delta^{11}\text{B}$  values of subduction inputs (pelagic sediments, trench turbidites, and altered oceanic crust) and subduction outputs (island arc lavas) suggests that little or no partitioning of boron isotopes occurs during the subduction process. In other words, the boron isotopic composition of the sediments and oceanic crust remains unchanged during subduction metamorphism, during transport of B from the slab into the arc magma source region, and during magma ascent and crystallization.

Several lines of evidence, however, suggest that the  $\delta^{11}\text{B}$  value of sediments and oceanic crust should decrease markedly during subduction as a result of progressive metamorphic dehydration reactions that preferentially remove  $^{11}\text{B}$  from the rock. Ishikawa and Nakamura (1993) have shown that ancient marine sediments have systematically lower  $\delta^{11}\text{B}$  values than modern sediments reflecting boron fractionation during diagenesis. Sediments beneath the Nankai subduction decollement have lower  $\delta^{11}\text{B}$  values ( $-12$  to  $-4$ ) than sediments above the decollement ( $-6$  to  $-2$ ) (You et al., 1995). Studies of natural metamorphic samples by Moran et al. (1992) and Bebout et al. (1993) clearly show that substantial amounts of boron are removed during prograde metamorphism, thus we would expect the  $\delta^{11}\text{B}$  val-

ues of metamorphic rocks to decrease with increasing metamorphic grade.

In order to better understand the boron cycle in subduction zones we used secondary ion mass spectrometry (SIMS) to determine the boron isotopic composition of minerals that formed during subduction-related metamorphism. We used SIMS for these analyses because we wanted to analyze small ( $< 30\ \mu\text{m}$ ) spots and preserve the textural information. If slab dehydration reactions fractionate boron isotopes, as predicted on theoretical and experimental grounds, we would expect the  $\delta^{11}\text{B}$  values of subduction-zone metamorphic rocks to be lower than those of sediments and altered oceanic crust. If slab dehydration reactions do not fractionate boron isotopes, then we would expect the  $\delta^{11}\text{B}$  values of subduction-zone metamorphic rocks to be similar to those of sediments and altered oceanic crust, and the slab melting hypothesis is strengthened.

### 3. SIMS analytical techniques

SIMS microanalyses were made with an approach similar to that used by Chaussidon et al. (1997); the entrance and exit slits of the mass spectrometer were closed slightly to separate  $^{10}\text{BH}^+$  from  $^{11}\text{B}^+$  and  $^{30}\text{Si}^{3+}$  from  $^{10}\text{B}^+$ . Using this approach, we have been able to measure  $^{11}\text{B}/^{10}\text{B}$  ratios with a precision of  $\pm 2\%$  ( $1\sigma$ ) at the 50–100 ppm level, and a precision of  $\pm 3\%$  at the 3–4 ppm level on 10–15  $\mu\text{m}$  diameter spots (precision can be improved on the high B concentrations by using longer analyses while analyses of the low-B samples required 3 h to obtain and could not be improved significantly without increasing the primary current intensity and thus the primary beam diameter to unacceptably large sizes). Beam diameters ranged from 15 to 30  $\mu\text{m}$  depending on the primary current used.

Calibration against known standards is critical for SIMS analyses. Chaussidon et al. (1997) studied a range of bulk-analyzed glasses and solutions by SIMS. The solutions were evaporated onto a Si wafer whereas glasses were mounted in epoxy and polished. These different samples showed no deviation from a single calibration (Chaussidon et al.,

1997). Our analyses of several bulk-analyzed minerals supports the observation by Chaussidon et al. (1997) that matrix effects are quite small. Our analyses for  $\delta^{11}\text{B}$  are calibrated against bulk-analyzed tourmaline (provided by Dr. W.P. Leeman, Rice University). Our SIMS analyses of the tourmaline yield  $^{11}\text{B}/^{10}\text{B}$  ratios approximately 40‰ lighter than the nominal ratio; similar to the results of Chaussidon et al. (1997).

#### 4. Subduction-related metamorphic rocks

We analyzed selected high-pressure minerals in well-characterized blueschists and eclogites from the Franciscan Complex and Catalina Schist (California) and a coesite-bearing eclogite from Dora Maira (western Alps) (Table 1). The metamorphic  $P$ – $T$  conditions represented by these samples are similar to those encountered by subducting oceanic crust and range from  $\sim 300^\circ\text{C}$  and 5–15 kbar (blueschists) to  $\sim 500^\circ\text{C}$  and 10–12 kbar (eclogites) to  $\sim 700^\circ\text{C}$  and  $> 30$  kbar (coesite eclogite). Detailed boron isotopic

studies of these samples, therefore, provide insight into the behavior of boron isotopes in the subducting slab down to depths of  $\sim 100$  km (Fig. 3).

We also analyzed subduction-related rocks from the Central Metamorphic Belt and Trinity peridotite (California) that form the lower and upper plates, respectively, of the Trinity thrust system (Davis et al., 1965; Peacock, 1987). The Central Metamorphic Belt consists of amphibolite-facies metabasalts and metasedimentary rocks which were thrust beneath the Trinity peridotite, one of the world's largest ultramafic massifs, during the Devonian Period (Davis et al., 1965; Peacock, 1987; Peacock and Norris, 1989). Metamorphism of the Central Metamorphic Belt was concurrent with thrusting and fluids released from dehydration reactions in the lower plate caused extensive serpentinization of the Trinity peridotite along the Trinity thrust (Peacock, 1987). The geologic relationships strongly suggest that the Central Metamorphic Belt represents a slice of oceanic crust subducted into the mantle, but it should be noted that subduction resulted in amphibolite-facies metamorphism rather than blueschist-facies metamorphism.

Table 1  
Sample descriptions and boron isotopic data

Sample number	Locality	Rock type	Metamorphic conditions	References	Mineral	$n$	$\delta^{11}\text{B}$	$1\sigma$
86-12C	Catalina Schist, California	Blueschist metagreywacke	$P = 12\text{--}15$ kbar; $T = 300^\circ\text{C}$	(1)	phengite	4	$-10.9$	1.8
TBE	Franciscan, California	Mafic eclogite	$P = 10\text{--}12$ kbar; $T = 500\text{--}540^\circ\text{C}$	(2)	phengite	9	$-2.7$	1.0
DR-182	Franciscan, California	Retrogressed mafic eclogite	$P = 9$ kbar; $T = 350\text{--}450^\circ\text{C}$	(3)	phengite	5	$-6.7$	1.9
82-DR-1	Franciscan, California	Actinolite rind, eclogite block	$P = 9\text{--}10$ kbar; $T = 300\text{--}350^\circ\text{C}$	(4)	phengite actinolite	3 7	$-7.0$ $-7.2$	1.7 3.0
A-38D	Dora Maira, Western Alps	Coesite eclogite	$P = 32\text{--}36$ kbar; $T = 700\text{--}750^\circ\text{C}$	(5)	phengite	9	$-6.1$	0.6
82-143A	Central Metam. Belt, California	Quartz schist	$P = 5 \pm 3$ kbar; $T = 550\text{--}650^\circ\text{C}$	(6)	muscovite	2	$-6.7$	2.0
82-257	Central Metam. Belt, California	Amphibolite	$P = 5 \pm 3$ kbar; $T = 550\text{--}650^\circ\text{C}$	(6)	hornblende	3	$-3.0$	3.0
YC-4	Trinity peridotite, California	Serpentinite	$T = 425\text{--}570^\circ\text{C}$	(7)	antigorite	4	$-10.4$	1.2

(1) Platt (1976); (2) Oh and Liou (1990); (3) Oh et al. (1991); (4) Moore (1984); (5) Schertl et al. (1991); (6) Peacock and Norris (1989); (7) Peacock (1987).

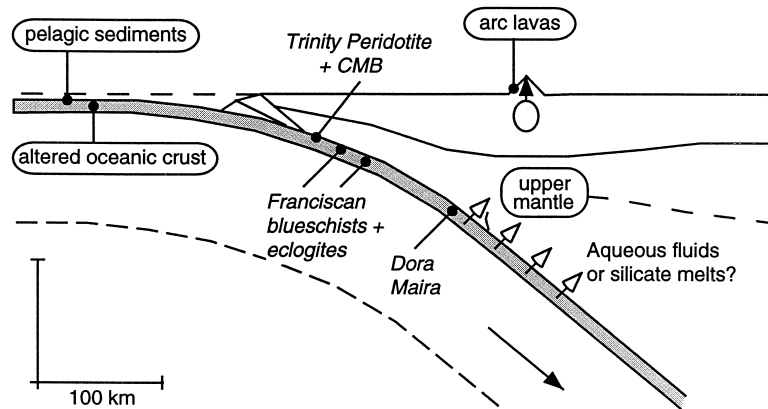


Fig. 3. Schematic cross section through a subduction zone showing relative positions of samples analyzed in this study based on peak metamorphic conditions and geologic relationships.

We focused our study on phengitic mica because previous work has shown phengite to be the most B-rich phase in high- $P$  metamorphic rocks (Domanik et al., 1993) and phengite is stable to depths of arc magma genesis (Domanik and Holloway, 1996). Because white mica dominates the boron budget (as well as other trace element budgets) of solid phases in the subducting slab (Domanik et al., 1993; Sorensen et al., 1997) the boron isotopic composition of phengite serves as an excellent proxy for the bulk slab. We also obtained SIMS analyses of amphibole in two samples (one with coexisting phengite) and serpentine in a hydrated peridotite.

## 5. Results

Phengite and actinolite from the high-pressure metamorphic rocks yielded  $\delta^{11}\text{B}$  values ranging from  $-11$  to  $-3$  (Table 1). Phengite in a blueschist-facies metagraywacke from the Catalina Schist yielded the lowest  $\delta^{11}\text{B}$  ( $-10.9 \pm 1.8$ ); primary phengite in a mafic eclogite from the Franciscan Complex showed the highest  $\delta^{11}\text{B}$  ( $-2.7 \pm 1.0$ ). Primary (?) phengite in the Dora Maira sample, which formed at depths  $> 90$  km, yielded a  $\delta^{11}\text{B}$  value of  $-6.1 \pm 0.6$ .

The  $\delta^{11}\text{B}$  values of phengite in the Franciscan Complex eclogites decrease with increasing degree of hydration. Primary phengite from the unretrogressed mafic eclogite (sample TBE) yielded  $\delta^{11}\text{B} = -2.7 \pm 1.0$ . In contrast, phengite from a hydrous

retrograde (?) vein in a mafic eclogite (sample DR-182) yielded  $\delta^{11}\text{B} = -6.7 \pm 1.9$ . Minerals from a metasomatic actinolite rind which formed around an eclogite block (sample 82-DR-1) yielded  $\delta^{11}\text{B} = -7.0 \pm 1.7$  (phengite) and  $\delta^{11}\text{B} = -7.2 \pm 3.0$  (actinolite).

Muscovite and hornblende from samples of the lower plate of the Trinity thrust system yielded  $\delta^{11}\text{B} = -6.7 \pm 2.0$  and  $-3.0 \pm 3.0$ , respectively. Antigorite that formed during serpentinization of the ultramafic upper plate of the Trinity thrust system yielded a significantly lower  $\delta^{11}\text{B}$  value of  $-10.4 \pm 1.2$ .

## 6. Discussion

### 6.1. Metamorphism of subducted sediments and oceanic crust

The  $\delta^{11}\text{B}$  values obtained from white mica, amphibole, and antigorite range from  $-11$  to  $-3$  (Table 1). These values are generally lower than  $\delta^{11}\text{B}$  values reported for pelagic sediments, trench turbidites, and altered oceanic crust (Fig. 2). It is possible that the relatively low  $\delta^{11}\text{B}$  values obtained in this study reflect low original  $\delta^{11}\text{B}$  values of the protolith, but the more likely explanation for the negative  $\delta^{11}\text{B}$  values is that metamorphic dehydration reactions have modified the boron isotopic composition of the rocks. In the following discussion we

assume that the  $\delta^{11}\text{B}$  values obtained in this study are a reasonable approximation of subduction-zone metamorphic rocks in general.

At equilibrium, aqueous fluids are enriched in  $^{11}\text{B}$  relative to minerals (Fig. 1). During progressive metamorphism, dehydration reactions should preferentially remove  $^{11}\text{B}$  thereby lowering the  $\delta^{11}\text{B}$  value of the rock. Fig. 4 illustrates how the boron isotopic composition of a rock and fluid may evolve during progressive metamorphism. In these examples the protolith  $\delta^{11}\text{B} = 0$  and boron is progressively removed from the rock by open-system Rayleigh distillation. The solid lines in Fig. 4 represent the case where the evolved fluid is enriched in  $^{11}\text{B}$  by a constant 10‰ relative to the rock. The dashed lines in Fig. 4 represent the case where the  $^{11}\text{B}$  enrichment of the fluid is a function of temperature (Oi et al., 1989; Fig. 1) and the rock is assumed to release fluids linearly between 25 and 725°C. The two models yield similar results — the progressive removal of boron from the rock decreases the  $\delta^{11}\text{B}$  values of the rock and the fluid. For example, the removal of 50% of the boron decreases the  $\delta^{11}\text{B}$  value of the rock from 0 to  $-8$ . The low  $\delta^{11}\text{B}$  values of subduction-zone metamorphic rocks observed in this study

are consistent with the isotopic depletions predicted by a boron isotope distillation model.

Possible  $\delta^{11}\text{B}$  values for aqueous fluids released from the slab may be bracketed by two sets of curves (Fig. 4). The "instantaneous fluid" curves represent the  $\delta^{11}\text{B}$  value of fluid in equilibrium with the rock at that particular instant; the "integrated fluid" curves represent the integrated (bulk)  $\delta^{11}\text{B}$  value of all fluid evolved up to that point. If all of the fluid released from the slab participates in arc magma genesis, then the "integrated fluid"  $\delta^{11}\text{B}$  curves are most relevant. Alternatively, if substantial amounts of fluids are released at shallow levels and escape to the surface, then the  $\delta^{11}\text{B}$  value of the fluid released from the slab at deeper levels will lie closer to the "instantaneous fluid"  $\delta^{11}\text{B}$  curves.

Samples in which the hydrous mineral is interpreted as having formed by reaction with an infiltrating aqueous fluid tend to have lower  $\delta^{11}\text{B}$  values and may reflect interaction with fluids derived from deeper levels of the subduction zone. In the Franciscan eclogite samples, phengite that formed in a hydrous retrograde (?) vein and in an actinolite rind yielded  $\delta^{11}\text{B} \sim -7$  as compared to  $-3$  for primary phengite. In the Trinity thrust system samples, the lowest  $\delta^{11}\text{B}$  value ( $-10$ ) was obtained from antigorite that formed as a result of infiltration of aqueous fluids into the base of the Trinity peridotite.

Previous studies have estimated the  $\delta^{11}\text{B}$  value of subducted sediments to be  $-8$  or  $-10$  (Ishikawa and Tera, 1997; Smith et al., 1997). These model values are lower than reported  $\delta^{11}\text{B}$  values for unmetamorphosed pelagic sediments and trench turbidites (Fig. 2), but are consistent with the lower  $\delta^{11}\text{B}$  values obtained from sediments that have undergone diagenesis (Ishikawa and Nakamura, 1993) or substantial dewatering during underthrusting (You et al., 1995). Thus, it seems generally accepted that the release of aqueous fluids from subducted sediments will decrease the  $\delta^{11}\text{B}$  value of the sediments. In contrast, previous studies do not appear to have considered the possibility that subducted basaltic oceanic crust will undergo a similar decrease in  $\delta^{11}\text{B}$  during slab metamorphism. For example, Ishikawa and Tera (1997) and Smith et al. (1997) estimated the  $\delta^{11}\text{B}$  value of subducted oceanic crust to be  $+8$  and  $+3.4$ , respectively, based on analyses of altered oceanic crust that did not experience prograde meta-

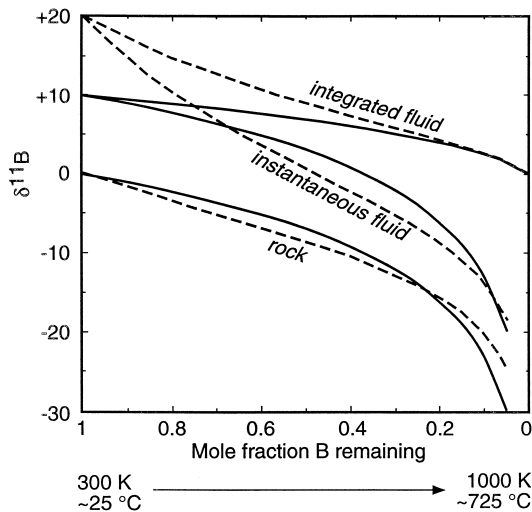


Fig. 4.  $\delta^{11}\text{B}$  values for rock, instantaneous fluid, and integrated fluid calculated for two different Rayleigh fractionation models. Solid lines, released fluid is enriched in  $^{11}\text{B}$  by 10‰; dashed lines,  $^{11}\text{B}$  enrichment of the released fluid is a function of temperature (Oi et al., 1989). Initial  $\delta^{11}\text{B}$  value of rock = 0. See text for discussion.



morphism. The metabasalt samples in this study have undergone subduction-zone metamorphism and yield  $\delta^{11}\text{B}$  values of  $-3$  to  $-7$ , substantially lower than those for altered oceanic crust. Our results suggest that subduction-zone metamorphic dehydration reactions will decrease the  $\delta^{11}\text{B}$  value of subducted oceanic crust as well as subducted sediments.

### 6.2. Generation of arc magmas

The  $\delta^{11}\text{B}$  values obtained from subduction-zone metamorphic rocks in this study are generally lower than  $\delta^{11}\text{B}$  values reported for island arc lavas (Fig. 2). Because the boron content of upper mantle is very low, most of the boron in arc magmas appears to be derived from the subducting slab. In order to derive the relatively high  $\delta^{11}\text{B}$  values ( $-6$  to  $+7$ ) observed in arc lavas from relatively low  $\delta^{11}\text{B}$  subduction-zone metamorphic rocks ( $-11$  to  $-3$ ) requires that boron isotopes are fractionated at some point between the slab and the eruption of the magma.

We suggest that boron isotopes are fractionated by metamorphic dehydration reactions and that boron is transferred from the slab to the arc magma source region by aqueous fluids as opposed to silicate melts. At 500 to 700°C, fluid coming off of the slab will be enriched in  $^{11}\text{B}$  by approximately 6 to 8‰ relative to the slab (Kakihana et al., 1977; Fig. 1). If subducted sediments and oceanic crust have  $\delta^{11}\text{B}$  values of  $-11$  to  $-3$  as observed in this study, then the fluid coming off the slab will have a  $\delta^{11}\text{B}$  value of  $-5$  to  $+5$  which overlaps most of the observed values for arc lavas. Fluids coming off the slab at shallower depths in the subduction zone and lower temperatures would have higher  $\delta^{11}\text{B}$  values. If the base of the hydrated mantle wedge is dragged down with the subducting slab (e.g., Tatsumi, 1989) then the relatively high  $\delta^{11}\text{B}$  fluids could be incorporated into arc magmas.

In contrast, we would not expect partial melting of the subducting slab to fractionate boron isotopes. Partial melts of subduction-zone metamorphic rocks would have the same range in  $\delta^{11}\text{B}$  values ( $-11$  to  $-3$ ) and therefore could not explain the majority of the published arc lava analyses that have  $\delta^{11}\text{B}$  values greater than  $-3$ .

## 7. Conclusions

SIMS analyses of minerals in subduction-zone metamorphic rocks yield  $\delta^{11}\text{B}$  values of  $-11$  to  $-3$  that are generally lower than the range of  $\delta^{11}\text{B}$  values reported for both subduction inputs (pelagic sediments, trench turbidites, and altered oceanic crust) and subduction outputs (island arc lavas). These data suggest that subduction-zone metamorphism significantly lowers the  $\delta^{11}\text{B}$  of subducted materials through continuous dehydration reactions. In order to explain the relatively high  $\delta^{11}\text{B}$  values observed in arc lavas as compared to subduction-zone metamorphic rocks, the B-bearing component derived from the slab must be enriched in  $^{11}\text{B}$  relative to the slab, which favors an aqueous fluid as the slab transfer mechanism.

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