

Record in metamorphic tourmalines of subduction-zone devolatilization and boron cycling

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ABSTRACT

Boron concentrations and isotope compositions of fluids and lavas from subduction-zone settings show great potential for elucidating mass flux at Earth's modern convergent margins. However, the fluid-mineral-melt behavior of B and its two stable isotopes remains relatively poorly understood. Boron isotope analyses of tourmaline in metasedimentary rocks subducted to 15–90 km depths (1) demonstrate the ability of this mineral to retain information regarding prograde devolatilization history in even highly retrograded rocks and (2) indicate the importance of tourmaline in affecting whole-rock B loss and B isotope evolution during subduction-zone metamorphism. The B lost from micas during metamorphism of subducting sedimentary rocks and altered oceanic crust is isotopically more enriched in ^{11}B than the B retained in the micas. Beneath forearcs and volcanic arcs, the B from micas is either removed from the subduction-zone rocks via metamorphic fluids or sequestered by growing tourmaline, in which the B can be entrained to even greater depths. Here we demonstrate that these metamorphic fluids could contribute to the relatively high $\delta^{11}\text{B}$ signatures observed in most arc lavas and the across-arc trends of decreasing $\delta^{11}\text{B}$ observed in several arcs.

Keywords: subduction zones, tourmaline, $^{11}\text{B}/^{10}\text{B}$, secondary ion mass spectrometry, metamorphism.

INTRODUCTION

Metamorphic rocks recrystallized at depth in subduction zones can yield detailed information regarding the chemical cycling that occurs at convergent margins. Studies of such suites (e.g., Bebout et al., 1999) have identified elements (e.g., B, Cs, As, Sb) that are mobilized significantly during subduction-zone metamorphism. These elements have been employed in attempts to trace additions from the subducting slab to the overlying mantle wedge, in which arc lavas are produced (e.g., Ishikawa and Nakamura, 1994; Ryan et al., 1995), and to trace sources of fluids in accretionary complexes (You et al., 1996). The element B has received particular attention because of its strong enrichment in sediments, hydrothermally altered oceanic crust, and H_2O -rich fluids thought to figure prominently in convergent-margin cycling (Ishikawa and Nakamura, 1994; You et al., 1996; Morris et al., 1990; Ishikawa and Tera, 1999; Benton et al., 2001). Studies of the stable B isotopes ^{11}B and ^{10}B afford further potential for tracing fluid-rock-melt processes. In subducting sediment and altered oceanic crust, B is thought to largely reside in minerals such as clays, micas, and tourmaline, the latter a borosilicate containing ~3 wt% B.

Subduction-zone metamorphic rocks are notorious for their superposition of retrograde assemblages produced during exhumation on prograde mineral assemblages produced during underthrusting. Tourmaline is a chemically robust phase capable of retaining information regarding protracted metamorphic histories (even premetamorphic history) in the form of chemical zoning and mineral inclusions—once formed, tourmaline does not readily readjust its composition by volume diffusion (Henry and Dutrow, 1996). The major and trace element and

B isotope compositions of tourmaline can thus aid in unraveling complex petrologic histories of deeply subducted rocks, in addition to elucidating the behavior and cycling of B in convergent margins. We obtained major element compositions (by electron microprobe) and B isotope compositions with high spatial resolution (10–15 μm , by ion microprobe methods of Nakano, 1998) for tourmalines in metasedimentary rocks of the Catalina Schist, California, United States, and from the coesite-bearing Lago di Cignana locality, Italy. Catalina Schist tectonometamorphic units represent peak metamorphism at depths corresponding to ~1.0 GPa, at temperatures of 350–650 °C (Grove and Bebout, 1995). At Lago di Cignana, metabasaltic and metasedimentary rocks were subjected to peak conditions of ~625 °C and 2.7–2.9 GPa, the latter indicating subduction to >90 km depths (Reinecke, 1998).

RESULTS

The Catalina metasedimentary suite and metasedimentary lithologies in the petrologically similar Sanbagawa belt (see petrologic synthesis by Nakano and Nakamura, 2001) show contrasting systematics in whole-rock B content and tourmaline abundance. The Sanbagawa metasedimentary rocks show uniform whole-rock B concentration across metamorphic grade, but with an increasing proportion of B residing in tourmaline and a decreasing proportion residing in micas at higher grades (Nakano and Nakamura, 2001). Catalina metasedimentary rocks contain far less tourmaline and at higher grades show a decrease in whole-rock B of as much as ~75% and a correlated decrease in mica B contents (Bebout et al., 1999). In both suites, some higher-grade (epidote-amphibolite) rocks contain abundant, zoned, dravitic tourmaline. In Catalina metasedimentary rocks, tourmaline cores have lower $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ and $\text{Ca}/(\text{Ca} + \text{Na})$ ratios and higher $\delta^{11}\text{B}_{\text{SRM951}}$ values (to +1.6‰, mostly –6‰ to –2‰, relative to the NIST SRM951 boric acid standard), and tourmalines show increased $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ (to 0.825) and $\text{Ca}/(\text{Ca} + \text{Na})$ and decreased $\delta^{11}\text{B}$ (approaching –15‰) toward rims (see Figs. 1A and 2). These major element variations are consistent with significant prograde tourmaline growth (Sperlich et al., 1996). Some of the higher-grade tourmalines have thin outermost zones, compositionally similar to cores, that we attribute to retrograde metamorphism (Fig. 2). The $\delta^{11}\text{B}$ values of less abundant tourmaline in lower-grade rocks (–7‰ to +4.5‰) overlap with, but are mostly higher than, the values of tourmaline cores in higher-grade rocks (Fig. 2A). The more abundant Sanbagawa metasedimentary tourmalines show similar core-to-rim variation in major element and B isotope compositions, but with less retrograded rims (Nakano and Nakamura, 2001).

Lago di Cignana metasedimentary rocks contain dravitic tourmaline (Fig. 1B), some with coesite inclusions (Reinecke, 1998), dramatically zoned in $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$, $\text{Ca}/(\text{Ca} + \text{Na})$, and $\delta^{11}\text{B}$ (example in Fig. 3). In these rocks, tourmaline cores with garnet and rutile inclusions have $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios to 0.95 and $\delta^{11}\text{B}$ values as low as –16‰; rims with clinozoisite and quartz inclusions have $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios as low as 0.55 and $\delta^{11}\text{B}$ values to +4.3‰. Tourmaline resembling the more colorful rims on prograde tourmaline, but occurring as separate grains, shows complex correlated zoning in $\delta^{11}\text{B}$ (with all values >0‰), $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$, and $\text{Ca}/(\text{Ca} + \text{Na})$.

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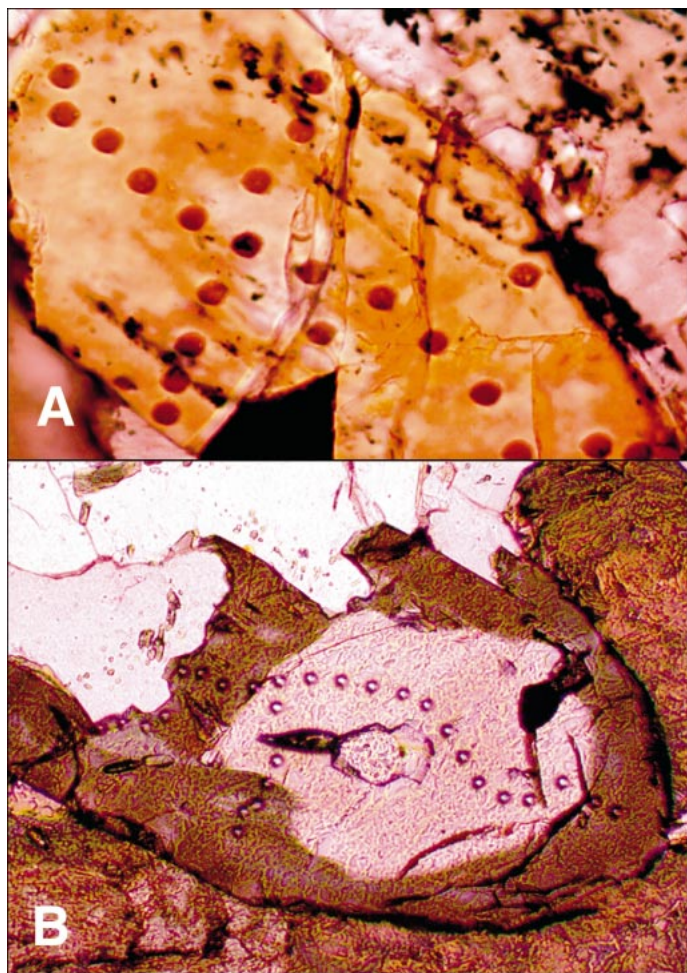


Figure 1. Photomicrographs, both in plane-polarized light, of chemically and isotopically zoned tourmaline in (A) Catalina metasedimentary sample at epidote-amphibolite grade (horizontal dimension corresponds to 200 μm) and (B) Lago di Cignana metasedimentary sample (horizontal dimension corresponds to 500 μm). Ion-microprobe pits are 10–15 μm in diameter.

DISCUSSION

Some key observations guiding consideration of the evolution of B isotopes in fluids and rocks during prograde devolatilization are that (1) the bulk of the tourmaline has low $\delta^{11}\text{B}$ values seemingly inherited from clays (the structurally bound sedimentary B component having isotopic values of -10% to -3% ; Spivack et al., 1987) and (2) the prograde trend in the Catalina and Sanbagawa tourmalines is from higher to lower $\delta^{11}\text{B}$ values, as deduced from the core-to-rim variations correlated with major element trends similar to those reported for other suites (Sperlich et al., 1996). B isotope fractionation is thought to be tied to the coordination of B in fluids, melts, and solids. The coordination of B is trigonal in both tourmaline and fluid, perhaps resulting in little fractionation between the two phases; however, the experiments of Palmer et al. (1992) suggested a possible P effect that warrants further investigation. B coordination is tetrahedral in melts, clays, and micas (for our rocks, phengitic white micas), and B having lower $\delta^{11}\text{B}$ values is thought to be preferentially incorporated into tetrahedral coordination ($\Delta^{11}\text{B}_{\text{fluid-mica}}$ is thought to be positive [Peacock and Hervig, 1999]; i.e., ^{11}B is preferentially fractionated into the fluids). Experimental work demonstrates that this fractionation is strongly temperature dependent and is $\sim +10\%$ at temperatures appropriate for the suites we studied (Hervig et al., 2002). The calculations presented in Figure 4A demonstrate that, with a $\Delta^{11}\text{B}_{\text{fluid-mica}}$ fractionation of $+10\%$, B release into fluids by devolatilization of micas would result

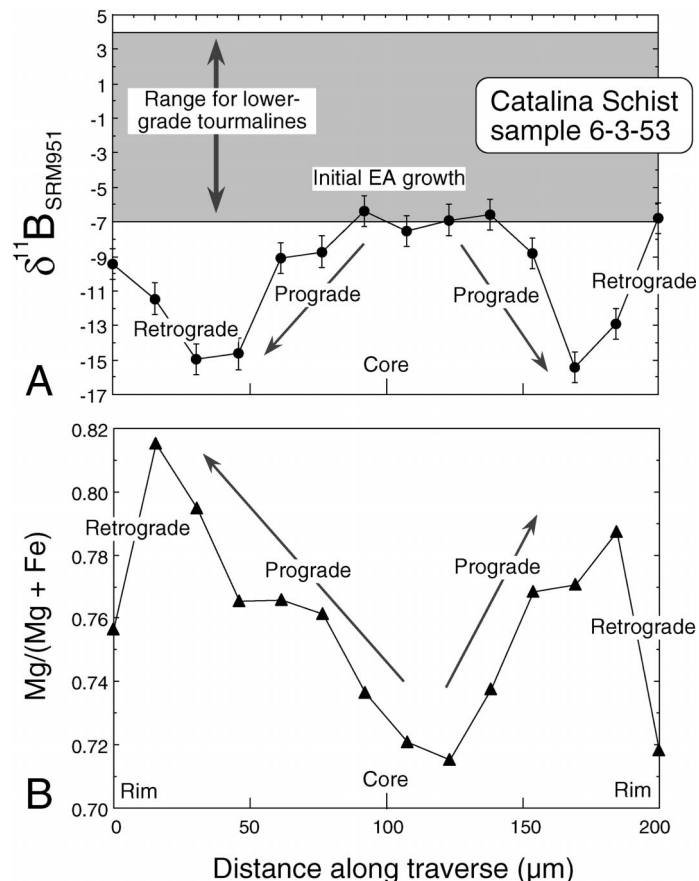


Figure 2. A: $\delta^{11}\text{B}$ values along core-rim-core traverse of Catalina tourmaline (Fig. 1A; traverse extending from upper left to lower right corners of photomicrograph), showing an interpretation of B isotope evolution of tourmaline in epidote-amphibolite (EA) grade Catalina metasedimentary rocks. Range of $\delta^{11}\text{B}$ in tourmaline from low-grade metasedimentary rocks is included for comparison. B: $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios along same traverse.

in a trend to lower $\delta^{11}\text{B}$ values in mica, fluid, and tourmaline, with progressive devolatilization of the micas, assuming no net loss of mica and concurrent growth of tourmaline. Depending on the B isotope fractionation between tourmaline and fluid, the $\delta^{11}\text{B}$ values of the tourmaline equilibrated with the ^{11}B -rich fluid released by micas would be either the same as the $\delta^{11}\text{B}$ values of the fluid or somewhat lower (Fig. 4A). We suggest that the core-to-rim zoning in tourmaline $\delta^{11}\text{B}$ (from near -6% to near -15% ; Fig. 2A) reflects sequestering by tourmaline of B evolving toward lower $\delta^{11}\text{B}$ values during progressive devolatilization (Fig. 4A).

The lowest-grade metasedimentary rocks in both the Sanbagawa and the Catalina suites have whole-rock $\delta^{11}\text{B}$ values in the range of -16% to -10% , similar to or lower than values for the structurally bound component in seafloor sediment (-10% to -3%). Sanbagawa metasedimentary rocks show no whole-rock B loss or shift in $\delta^{11}\text{B}$ with increasing grade, observations consistent with a model in which any B lost from micas was incorporated into growing tourmaline (Nakano and Nakamura, 2001). In the Catalina suite, which for the most part lacks tourmaline, one would expect to see a whole-rock trend of decreasing $\delta^{11}\text{B}$, with increasing devolatilization, reflecting evolution in the $\delta^{11}\text{B}$ values of mica, the only significant B host (see curve labeled "mica sediment" in Fig. 4A). However, several higher-grade Catalina metasedimentary rocks have whole-rock $\delta^{11}\text{B}$ values higher than those of lower-grade equivalents (to -1% ; Nakano, 1998), and these higher values are thought to reflect the $\delta^{11}\text{B}$ of abundant retrograde white mica. Thus, in higher-grade Catalina rocks, tourmaline

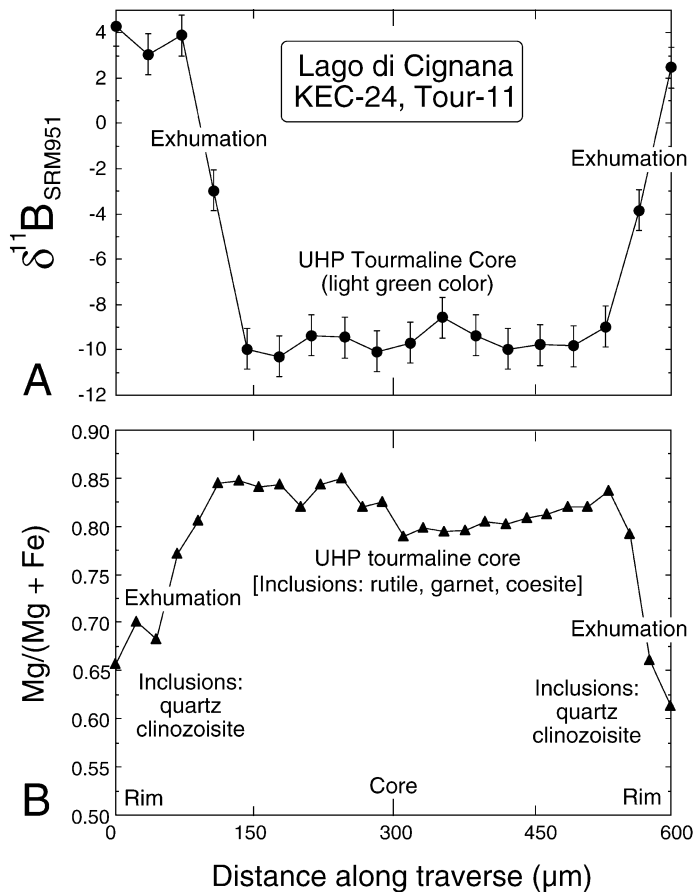


Figure 3. A: Plot demonstrating strong $\delta^{11}\text{B}$ zonation in Lago di Cignana tourmaline (Fig. 1B; along roughly horizontal traverse in photomicrograph), showing abrupt change in $\delta^{11}\text{B}$ from light colored core region to strongly colored rim. **B:** $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ along same traverse. UHP—ultrahigh pressure.

(other than the outermost zone attributed to retrograde metamorphism; Fig. 2) contains the most reliable record of prograde B isotope evolution.

In the Lago di Cignana metasedimentary rocks, individual tourmalines do not appear to preserve prograde B evolution in the form of B isotope zonation, perhaps as a result of recrystallization and homogenization at the higher temperatures that have affected these tourmalines ($\sim 630^\circ\text{C}$). The overall variation in the B isotope compositions of the tourmalines appears to reflect (1) prograde incorporation of B with $\delta^{11}\text{B} = -13\text{‰}$ to -9‰ into the tourmaline with high $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios and containing inclusions of coesite, rutile, and Mg-garnet, and (2) the incorporation, during exhumation, of B with $\delta^{11}\text{B} > 0\text{‰}$ into strongly colored tourmaline with lower $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratios and containing inclusions of clinozoisite and quartz. The presence of prograde tourmaline with the low $\delta^{11}\text{B}$ values (-15‰ to -10‰) indicates deep subduction, in tourmaline, of B initially subducted in seafloor sediments.

At shallow levels of subduction zones, adsorbed B with high $\delta^{11}\text{B}$ is lost from subducting sediments, leaving the structurally bound B with $\delta^{11}\text{B}$ of -10‰ to -3‰ . This relatively ^{11}B -rich “desorbable” B (with $\delta^{11}\text{B}$ of $+14\text{‰}$ to $+16\text{‰}$; You et al., 1996; Spivack et al., 1987), together with the relatively ^{11}B -rich B expected as the result of initial devolatilization in shallow levels of subduction zones, might lead to the high $\delta^{11}\text{B}$ values (to $+13\text{‰}$; some higher values reflect shallow mixture with seawater and changes in pH) of serpentinite seamounts in the Mariana forearc (Benton et al., 2001). The processing of B in forearcs (at 10–50 km) involves gradual transfer of structurally

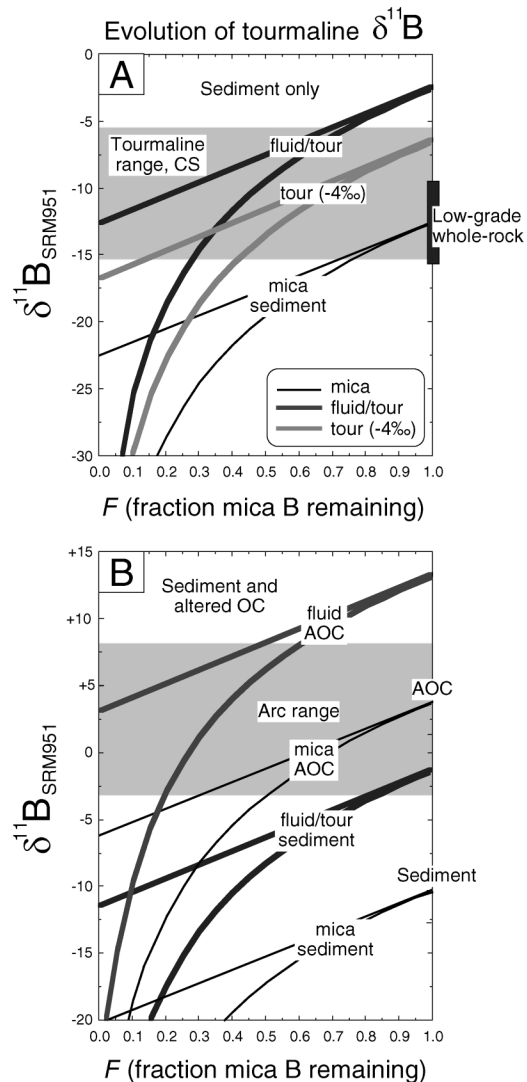


Figure 4. Calculations demonstrating possible evolution in B isotope compositions of micas, fluids, and tourmaline in progressively metamorphosing, subducting sediments and altered oceanic crust (AOC). In these calculations, $+10\text{‰}$ $\Delta^{11}\text{B}$ fractionation between fluid and mica is applied (see Hervig et al., 2002), and $\Delta^{11}\text{B}$ fractionation between tourmaline (tour) and fluid is assumed to be either 0‰ or $+4\text{‰}$. Shown in these figures are calculations for both Rayleigh model (curves) and batch-volatilization model (straight lines). **A: Demonstration that progressive uptake of B relatively rich in ^{11}B that was lost from micas could produce B isotope compositions observed in isotopically zoned tourmalines in Catalina and Sanbagawa (CS) metasedimentary rocks. Core-to-rim decrease in $\delta^{11}\text{B}$ could reflect evolution in $\delta^{11}\text{B}$ values of B released from micas during progressive devolatilization (see parallel evolution in $\delta^{11}\text{B}$ of residual B in micas). Ion-microprobe analyses of B contents in white micas in Catalina metasedimentary rocks indicate decrease in mean B concentration from 165 ppm in lowest-grade rocks to 50 ppm in higher-grade rocks (epidote-amphibolite facies), suggesting $\sim 70\%$ loss, or $F = 0.30$. **B:** Illustration of similar evolution in $\delta^{11}\text{B}$ expected for AOC, in which mica is similarly thought to be primary B host. Data for AOC are from Smith et al. (1995). Differential mixing of fluid derived from progressively devolatilizing sediment and AOC could in part produce range and across-arc trend in $\delta^{11}\text{B}$ observed in some arcs.**

bound B in clay into low-grade white micas, perhaps accompanied by some loss of ^{11}B to fluids and resulting in some shift in subducting rocks toward lower $\delta^{11}\text{B}$ values (evidenced by values of -16% to -8% for the lowest-grade Catalina Schist and Sanbagawa metasedimentary rocks; Nakano, 1998; cf. Peacock and Hervig, 1999). Tourmaline growth at these and greater depths, which will strongly affect the extent to which sedimentary B is more deeply subducted, could depend on a number of factors, including bulk-rock and fluid chemistry (Henry and Dutrow, 1996; Schreyer and Werdning, 1997), pressure-temperature path (Bebout et al., 1999), and the presence or absence of detrital tourmaline as seed crystals for further growth (see Henry and Dutrow, 1996).

Ishikawa and Tera (1999) suggested that varying sediment/altere oceanic crust ratios along the Mariana arc produced differences in the compositions of fluids contributed to the subarc mantle wedge and proposed that Mariana lavas had 95% or greater fluid contributed from altered oceanic crust. Tourmaline is rare in subduction-zone metamorphosed metabasaltic rocks (Nakano, 1998), and it is likely that the B inventory in such rocks is governed by the abundance of mineral phases such as the micas. These micas would be expected to fractionate B isotopes with aqueous fluids in the same way as micas in metasedimentary rocks—B isotope compositions of fluids and residual B in micas would fractionate along curves similar to those in Figure 4A, but displaced to somewhat higher $\delta^{11}\text{B}$ values owing to the higher starting $\delta^{11}\text{B}$ values of the altered oceanic crust (mean values near $+4\%$, higher than values for metasedimentary mica; see Fig. 4B). Mixing, in differing proportions, of fluids derived from subducting sediment and oceanic crust would be capable of producing the ranges of $\delta^{11}\text{B}$ values in some arcs, and the cross-arc decline in $\delta^{11}\text{B}$ noted in several arcs could in part reflect progressive lowering of rock (and fluid) $\delta^{11}\text{B}$ values during devolatilization (trends in Fig. 4B). Our results demonstrate a fractionation process by which subducting materials could deliver a B isotope fluid composition that evolves with increasing depth, thus providing a mechanism by which across-arc B isotope variation can be explained largely by slab B isotope fractionation without invoking varying mixtures of slab-derived fluids of fixed B isotope composition with fluids evolved in the hydrated mantle wedge (see contrasting interpretations by Ishikawa et al., 2001; Straub and Layne, 2002). In warm arcs and some backarc regions, silicate melts produced by melting of subducting rocks could inherit the $\delta^{11}\text{B}$ values of mica previously isotopically shifted by devolatilization and the low $\delta^{11}\text{B}$ values of tourmaline that sequestered the sedimentary B previously released from micas. Transfer of these melts to the subarc mantle wedge could result in lavas with relatively low $\delta^{11}\text{B}$ (Rose et al., 2001).

As demonstrated by the comparisons of B behavior in the Catalina and Sanbagawa suites, whether tourmaline nucleates and grows in subducting sediments (and altered oceanic crust) is likely a key factor in determining the B isotope evolution of the rocks (and fluids released from these rocks), and in producing the record of slab B inputs in arc volcanic suites. Tourmaline growth in deeply subducting lithologies can presumably also strongly influence the fraction of initially subducted B that enters the deeper mantle beyond subarc regions. This study showcases the ability of tourmaline to preserve records of chemical and isotopic redistribution despite extensive exhumation-related, retrograde overprinting characteristic of high- and ultrahigh-pressure metamorphic suites.

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