

Boron and lead isotope signatures of subduction-zone mélange formation: Hybridization and fractionation along the slab–mantle interface beneath volcanic arcs

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Abstract

The B and Pb isotope systems are widely applied tracers of recycling processes occurring during subduction. Studies examining these complementary systems as a pair enjoy considerable success, where B primarily records the thermal and fluid evolution of the subducting slab, whereas the tripartite Pb system constrains the source of subducted material returned to volcanic arcs. However, interpretations derived from the arc volcanic record critically depend upon assumptions regarding compositions of unmetamorphosed inputs to subduction zones. Few studies have directly addressed potential fractionation of B isotopes and U–Th–Pb by analysis of high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic suites, despite that fractionation in these systems during subduction-zone metamorphism has been inferred in many studies of volcanic arcs and ocean–island basalts. Here, we address the metamorphic evolution of subducted material with B and Pb isotope determinations for the mélange matrix of the Catalina Schist, CA.

Within the Catalina Schist, mélange matrix formed through the synergistic effects of metasomatism and deformation, affecting basalts and sediments derived from the subducting Farallon plate with peridotites derived from the overlying mantle wedge. Models of simple mechanical mixing among these end-members broadly predict both B and Pb concentrations within hybridized schistose mélange matrix, but an explanation of isotope ratios for both systems requires significant fractionation during metamorphism. The B isotope results are compatible with the previously presented model for sources and transport of fluid within the Catalina Schist subduction zone based on O and H isotope data: $\delta^{11}\text{B}$ values for the amphibolite facies mélange matrix are consistent with infiltration by B-bearing fluid produced in lower-T metasediment-rich domains, whereas the lower-grade lawsonite–albite and lawsonite–blueschist tectonometamorphic units represent possible analogs for the sources of this B-bearing fluid. Overall, Pb isotope ratios are indistinguishable as a function of metamorphic grade and are highly radiogenic. We constrained the potential influence of radiogenic continental detritus to the Catalina subduction zone by estimation of the continental input component from detrital zircon U–Pb age spectra. This zircon-based sedimentation proxy demonstrates that the potential influence of the Mesozoic California Andean-type convergent margin cannot in all cases explain the radiogenic Pb signature of the Catalina

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mélange matrix, seemingly requiring some fractionation of the U–Th–Pb system during formation of the lawsonite–albite and lawsonite–blueschist mélange units. Pb isotope signatures of the lower-grade mélange matrix can be explained by a two-stage metamorphic fractionation model involving early loss of Pb by desulfidation reactions, followed by deeper loss of silicate U, during subduction. Pb signatures of the amphibolite facies mélange matrix suggest either efficient retention of protolith Pb signatures during metamorphism or faithful transfer of the fractionated Pb signature by metamorphic fluid flow. Contamination of the mantle wedge by Catalina Schist B and Pb isotope fluid signatures can explain B–Pb isotope anomalies observed for modern arcs, indicating that the effects of mélange mixing should be considered in models of subduction-zone mass transfer.

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1. Introduction

A long-standing goal of subduction zone research is to determine how subducted mass is redistributed between crustal and mantle reservoirs. The readily targeted “inputs” to this process include oceanic crust, pelagic sediment, and trench-fill detritus (e.g. Smith et al., 1995; Rea and Ruff, 1996; Plank and Langmuir, 1998; Hauff et al., 2003; Kelley et al., 2003). Similarly, the easily accessed “outputs” of the subduction process are the compositions of arc volcanic rocks and ocean island basalts (e.g. Ishikawa and Nakamura, 1994; Pearce and Peate, 1995; Ryan et al., 1995; Elliot et al., 1997; Ishikawa and Tera, 1999; Rosner et al., 2003; Moriguti et al., 2004; Kelley et al., 2005). Comparison of the inputs and outputs of the subduction process has given rise to explicit predictions regarding the role of metamorphic processes in redistributing subducted mass between the crust and mantle during subduction (e.g., Chauvel et al., 1995; Bach et al., 2003; Kelley et al., 2005). To evaluate these predictions, it is necessary to directly examine subduction zone rocks for evidence of how mass is redistributed during metamorphism (e.g. Sorensen and Barton, 1987; Bebout, 1991, *in press*; Bebout and Barton, 1989, 1993; Sorensen and Grossman, 1989, 1993; Bebout et al., 1993, 1999, 2007-*this issue*; Zack et al., 2002; Chalot-Prat et al., 2003; Spandler et al., 2003, 2004; King et al., 2003, 2004, 2006; Marschall et al., 2006, 2007-*this issue*; Zack and John, *this volume*).

Boron and Pb isotope systematics have proven to be of great value in studies undertaken to address recycling of subducted mass back into the crust. Although B and Pb are equivalently mobile in slab-derived fluids, the processes that govern their mobility appear to differ significantly. For example, redistribution of B and fractionation of its isotopic species is known to be a strong function of the thermal evolution and resulting devolatilization history of subducted materials (e.g., Moran et al., 1992; Bebout et al., 1993,

Peacock and Hervig, 1999; Nakano and Nakamura, 2001; Bebout and Nakamura, 2003; Marschall et al., 2007-*this issue*). Alternatively, whereas Pb isotopic data are widely believed to preserve the signature of the subducted protolith (e.g., Hauff et al., 2003), few studies have explicitly examined this (Usui et al., 2006). This is unfortunate, particularly in light of predicted metamorphic U–Th–Pb fractionation during subduction (Chauvel et al., 1995; Bach et al., 2003; Kelley et al., 2005).

There is growing appreciation that mass transfer within enhanced permeability structures such as mélange zones and fracture systems may dominate slab-derived signatures transferred to the mantle wedge (Bebout and Barton, 2002; Breeding et al., 2004; John et al., 2004; King et al., 2006; Ague, 2007-*this volume*; Zack and John, 2007-*this volume*) relative to the impact of less-deformed subducted lithologies (e.g., Chalot-Prat et al., 2003; Spandler et al., 2003, 2004; Spandler and Hermann, 2006). Based on extensive O–H–N isotopic study, mélange zones have been shown to represent zones of greatly enhanced fluid flow that are characterized by pervasive stable isotope homogenization and extensive redistribution of many major and trace elements (Bebout, 1991, 1997; Bebout and Barton, 1993, 2002). In this paper, we examine the B and Pb isotopic systematics of mélange present within a deep-seated accretionary complex (Catalina Schist, CA, USA) to gain insights into the evolution of these systems during subduction. In our consideration of Pb isotope behavior in these units, we utilize detrital zircon U–Pb age distributions (Grove et al., *in press*) to help us deduce the time-dependent variation of the Pb isotopic composition of trench-fill sediment derived from the adjacent mid-Cretaceous arc and continental domain. These data help us to resolve the disparate behavior of the B and Pb isotope systems during subduction metamorphism, allowing for a more complete view of how these geochemically important tracers are redistributed during subduction.

2. Mélange matrix of the Catalina Schist

The Catalina Schist is a mid-Cretaceous accretionary complex that crops out in the offshore region of southern California (Platt, 1975). Exposures on Santa Catalina Island consist of successively accreted, tectonic sheets that define an inverted metamorphic sequence from amphibolite to lawsonite–albite facies (Grove and Bebout, 1995; Grove et al., in press). The structurally highest amphibolite facies rocks are dominated by ultramafic and mafic lithologies with minor chert and craton-derived greywacke that collectively record anatectic conditions of 600–750 °C and 0.8 to 1.3 GPa (e.g., Sorensen and Barton, 1987). Available thermochronology indicate protracted high-grade conditions in which the rocks resided above 500 °C between ~115–108 Ma (Suppe and Armstrong, 1972; Mattinson, 1986; Grove and Bebout, 1995; Anczkiewicz et al., 2004; Grove et al., in press). In contrast, the structurally lowest lawsonite–blueschist and lawsonite–albite rocks were accreted much later (~100–95 Ma) and cooled much more rapidly. These lower grade rocks are dominated by plutonic and volcanic arc-detritus derived from the adjacent Peninsular Ranges batholith but also contain subordinate, though locally abundant, mafic and ultramafic lithologies. Although most studies of the Catalina Schist have considered that all rocks were accreted within the subduction zone (e.g., Platt, 1975; Sorensen and Barton, 1987; Grove and Bebout, 1995; Bebout and Barton, 1989, 1993, 2002), Grove et al. (in press) have proposed that the amphibolite facies rocks may actually represent forearc basement that was underthrust to subcrustal depths beneath the western margin of the mid-Cretaceous Peninsular Ranges batholith and later juxtaposed with the accretionary complex as a result of continued shortening in the forearc region by 95 Ma. Hence the Catalina Schist may actually represent the cumulative product of processes active throughout the entire forearc region rather than within a narrow zone localized above the subducting slab.

An essential characteristic of the Catalina Schist is the ubiquitous occurrence of prograde mélange that alternates with, and envelops, more structurally intact and compositionally homogeneous lithologies. Mineral assemblages constraining metamorphic conditions within the mélange are, in general, isofacial with those contained within adjacent, less deformed rocks (Platt, 1975; Sorensen and Barton, 1987; Bebout and Barton, 1989; Grove and Bebout, 1995). This situation contrasts with the occurrence of exotic blocks in mélange that characterizes some shallow subduction complexes such as the Franciscan Complex. In the

latter, blocks characteristically have experienced a metamorphic evolution unrelated to their matrix host (e.g., Cloos and Shreve, 1988; King et al., 2003; Saha et al., 2005). Clearly exotic, higher-grade blocks appear to be rare within the Catalina Schist (e.g., Grove and Bebout, 1995; Anczkiewicz et al., 2004) although they do occur along major faults bounding individual tectonic sheets (Platt, 1975). Throughout this contribution we use the term “mélange matrix” for schistose rocks consisting of hybridized bulk-rock compositions resulting from mechanical and metasomatic mixing between peridotite, basaltic, and sedimentary protoliths (see also Bebout and Barton, 1993, 2002; King et al., 2006). The term “coherent block” designates much less deformed lithologies encased in the mélange that have recognizable protoliths (e.g., metasediments, metabasalts, metaperidotites).

It is important to emphasize that the scale of some mélange zones within the Catalina Schist is similar to that of altered oceanic crust and overlying sediment (see Bebout and Barton, 2002, for mélange mapped at the kilometer scale). Altered oceanic crust is largely confined to the upper 1 km of subducting oceanic lithosphere and sea-floor sediment, though widely variable, is generally <400 m (Plank and Langmuir, 1998). In spite of the similarity of scale, significant compositional variation of the mélange does occur throughout the Catalina Schist. For example, amphibolite facies mélange matrix dominated by ultramafic and mafic bulk compositions whereas lawsonite–albite and lawsonite–blueschist mélange is enriched in plutonic and volcanic arc detritus relative to ultramafic and mafic lithologies (Bebout and Barton, 1993, 2002; King et al., 2006). In an effort to adequately represent compositional variation throughout the mélange, we analyzed a large population of mélange matrix samples formed at three metamorphic grades for major and trace elements ($n=58$), with representative subsets for Pb ($n=28$) and B ($n=24$) isotopes. Samples of mélange were collected from zones of lawsonite–albite facies conditions of 150–250 °C, 0.3–0.7 GPa (herein referred to as “LA mélange”; total $n=16$, Pb $n=7$, B $n=6$), lawsonite–blueschist facies conditions of 200–350 °C, 0.7–1.0 GPa (“LB mélange”; total $n=23$, Pb $n=10$, B $n=9$), and amphibolite facies conditions of 600–750 °C, 0.8–1.3 GPa (“AM mélange”; total $n=19$, Pb $n=11$, B $n=9$).

In general, the AM mélange matrix is much more ultramafic than the more “crustal” Si- and Al-rich LA/LB mélange (Bebout and Barton, 2002; King et al., 2006). Comparison of B and Pb concentrations to MgO (Fig. 1) illustrates hybridization behavior typical of

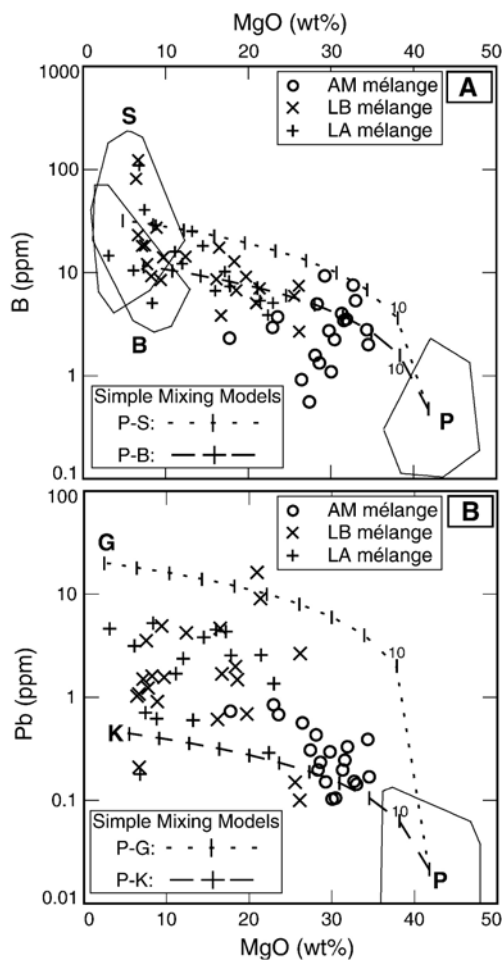


Fig. 1. Variation in B (panel A, above) and Pb (panel B, below) within the mélange matrix of the Catalina Schist as a function of bulk composition (proxied by MgO). Reference compositions used to represent likely sources of mass from blocks in mélange are shown as bold letters: P, Horoman Peridotite Complex of Japan (Yoshikawa and Nakamura, 2000; Tanimoto, 2003); S and B, sedimentary and basaltic blocks, respectively, of the Catalina Schist (Bebout et al., 1993, 1999); K, the altered oceanic crust composite of Kelley et al. (2003); G, the estimated composition of global subducting sediment (GLOSS) of Plank and Langmuir (1998). Ideal mechanical mixing is modeled by simple mixing of peridotite with basalt/AOC (dashed lines) and peridotite with sediment/GLOSS (dotted lines). Vertical tick marks for all mixing models indicate 10% increments of mixing; ticks representing only the first 10% addition of any other end-member to peridotite are labeled to simplify the diagram.

mélange matrix and the major distinctions of AM vs. LA/LB mélange. Hybridization in the mélange matrix is a function of both the mechanical mixing that probably dominates mélange formation (illustrated in Fig. 1 and following figures as simple mixing models), as well as metasomatic fluid flow and phase stability of mineral hosts during metamorphism (Bebout and Barton, 1993, 2002; King et al., 2006).

3. Methods

This study presents B and Pb isotope ratios for whole-rock samples of the mélange zones of the Catalina Schist. All isotope analyses were performed at the Pheasant Memorial Laboratory, Okayama University at Misasa, Japan. Methods and data for elemental geochemistry of the Catalina Schist mélange matrix are presented in King et al. (2006).

B isotope ratios were measured using thermal ionization mass spectrometry (TIMS) by the HF–mannitol– Cs_2BO_2^+ method (Nakamura et al., 1992; Nakano and Nakamura, 1998). B isotope ratios of unknowns are presented as $\delta^{11}\text{B}$ values relative to the B isotope standard SRM951, measured concurrently ($^{11}\text{B}/^{10}\text{B} = 4.0491 \pm 0.0011$ [1σ], $n=19$). SRM951 was analyzed both from unmodified stock solution ($^{11}\text{B}/^{10}\text{B} = 4.0491 \pm 0.0011$ [1σ], $n=9$) as well as after complete chemistry used for unknowns ($^{11}\text{B}/^{10}\text{B} = 4.0490 \pm 0.0011$ [1σ], $n=10$). Samples were prepared for B chemistry by digestion of sufficient powdered sample to yield 1 μg of B in the final solution. Mannitol solutions were used continuously during chemistry as the B–mannitol complex effectively prevents B volatility (Nakamura et al., 1992). B chemistry was performed in the B-free, over-pressured air system at the PML, which allows for negligible B blanks (mean = 4.076 ± 0.813 ng B [1σ], $n=7$); blanks were sufficiently small to be ignored and no blank corrections were made. Duplicate chemistry and mass spectrometry was performed for every unknown. The overall uncertainty of the method is $\pm 0.3\%$.

Samples were prepared for Pb chemistry by digestion of 50–300 mg of powdered whole rocks within Teflon bombs. A sufficient volume of twice-distilled, concentrated HF was added to each bomb and samples were digested at 205 °C for three to four days. Following digestion samples were transferred to Teflon beakers and a volume of twice-distilled HBr equal to the volume of HF was added to the solution, and samples were heated for ~ 24 h to produce Pb–bromide complexes for column chemistry. Pb was sequentially separated from solution using two-stage column chemistry as described by Kuritani and Nakamura (2002). Pb yields were measured using ICPMS to ensure proper spiking; Pb yields were typically 30–60% of ideal sample concentrations. Pb isotope ratios were measured by TIMS using double-spike methods. Most samples were measured using a “normal” double-spike technique consisting of an unspiked run and a ^{207}Pb – ^{204}Pb spiked run. Final samples with extremely low Pb concentrations (3 of 28) were measured using the “two double-spikes” technique, in

which the unspiked run of the normal double-spike method is augmented with a ^{205}Pb – ^{204}Pb spike for improved precision at small sample sizes (Kuritani and Nakamura, 2003). Repeated measurement of Pb standard NBS981 over the course of this study ($n=9$) yielded measured ratios indistinguishable from reported values (cf. Kuritani and Nakamura, 2003). Average ratios and errors (2σ) for NBS981 were: $^{206}\text{Pb}/^{204}\text{Pb}$, 16.9417 ± 0.0021 ; $^{207}\text{Pb}/^{204}\text{Pb}$, 15.4993 ± 0.0021 ; $^{208}\text{Pb}/^{204}\text{Pb}$, 36.7240 ± 0.0049 .

4. B geochemistry

Fig. 2 presents elemental B–Th–Li systematics useful for interpretation of B isotope ratios. The observed behavior of B, Th, and Li within the mélange is likely controlled by the stability of important host phases. Under the metamorphic conditions represented by the Catalina Schist, B is expected to reside largely within mica (similar to Rb, Cs, and Ba; Marschall et al., 2006, 2007-this issue; Bebout et al., 2007-this issue) while Li is hosted primarily by Mg-rich chlorite and/or mica (Marschall et al., 2006, 2007-this issue; Bebout et al., 2007-this issue), and Th is mainly contained within phosphates or the epidote-group minerals (Hermann, 2002; Zack et al., 2002; Spandler et al., 2003). Within Fig. 2, the positive correlation of B/Th or B/Li with increasing B concentration that is exhibited by the low-grade mélange units can be understood in terms of B loss via mica devolatilization (King et al., 2006; Moran et al., 1992; Marschall et al., 2007-this issue) or effective diffusive partitioning from mica to attending metamorphic fluids (Schmidt and Poli, 2003). Because mica is absent within the AM mélange, the correlation between B/Th and B/Li is poor (see King et al., 2006). Note however, that the AM mélange yields higher B/Th or B/Li ratios at a given B concentration. Because B concentrations for AM mélange are low, the comparatively higher B/Li and B/Th ratios of AM mélange as compared to LA/LB mélange is an important observation that appears to imply fluid-related addition of B to the AM mélange.

Fig. 3 presents $\delta^{11}\text{B}$ data for the mélange (see online dataset). The overall variation of $\delta^{11}\text{B}$ as a function of B concentration is presented in Fig. 3A. Low-grade LA and LB mélange matrices preserve negative $\delta^{11}\text{B}$ ranging from -2.3 to -12.0% , whereas AM mélange records distinctly elevated ratios of $+3.7$ to -3.3% . Closer inspection of LA mélange results reveals that $\delta^{11}\text{B}$ covaries with B concentration, B/U, and age-corrected metamorphic $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (Fig. 3B–D). We interpret this behavior as a consequence of mechanical

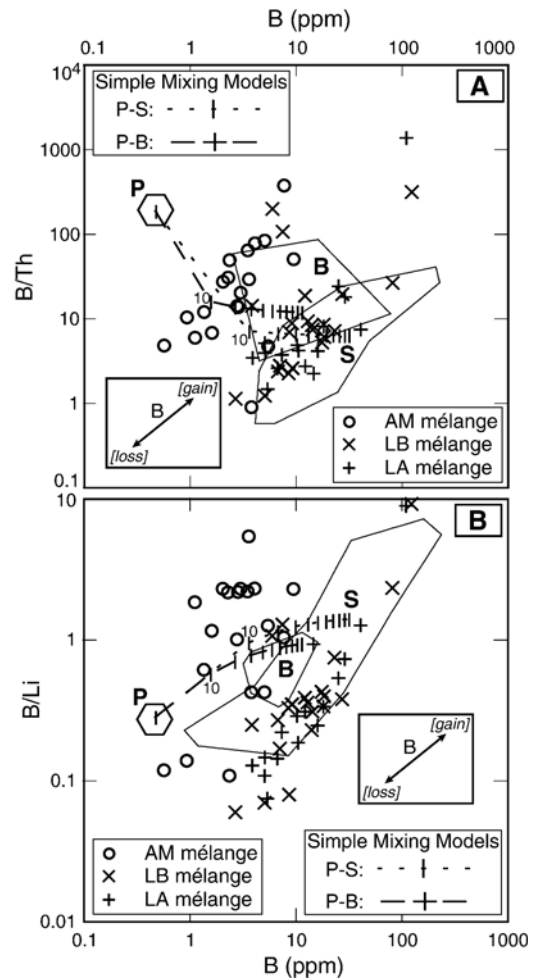


Fig. 2. Variations in B/Th (panel A, above) and B/Li (panel B, below) as a function of B concentration in mélange matrix of the Catalina Schist. The choices of Th and Li as normalizing agents for B are meant to illustrate how petrogenesis of mélange matrix may preferentially affect variations in B concentration as compared to: [1] those expected for melting of the mantle, where B and Th have similar solid/liquid partitioning coefficients; or [2] potential differences in fluid mobility of B and Li during metamorphism, where abundances of these light elements are controlled by different minerals with distinct solid/fluid partitioning during metamorphism (Marschall et al., 2007-this issue). Fields, symbols, and simple mixing models are identical to Fig. 1A; additionally, inset arrows illustrate vectors for B gain/loss expected for metasomatic fluid flow. The hexagon labeled P is an approximate composition for peridotite, as no single study for the Horoman Complex has analyzed B, Th, and Li for the same samples. For the peridotite mixing end-member, Th and Li data are from Tanimoto (2003), B data are from Yoshikawa and Nakamura (2000).

mixing affecting the LA mélange. This is important in that it implies that deformation is a more important control on B geochemistry than is metasomatic fluid flow at the metamorphic conditions that attended formation of the LA mélange. Note that the apparent mixing

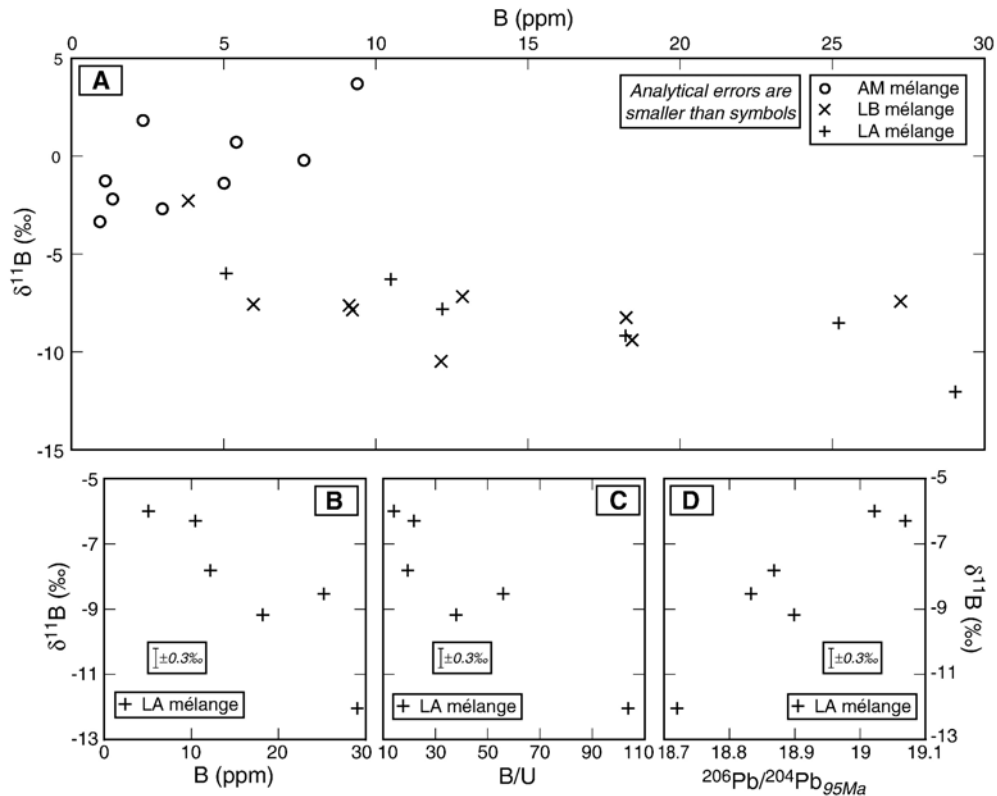


Fig. 3. Comparison of $\delta^{11}\text{B}$ to element and isotope variations within Catalina Schist mélanges matrix. Above, panel 3A presents variation of $\delta^{11}\text{B}$ as a function of B concentration for all analyzed samples. Lower-grade LA and LB mélanges matrices record high B concentrations at depleted isotope ratios, whereas low B concentrations of AM mélanges matrix are associated with comparatively enriched $\delta^{11}\text{B}$. Below, panels 3B–D illustrate apparent mixing behavior preserved within lowest-grade LA-facies mélanges matrix. Approximately linear trends between $\delta^{11}\text{B}$ and B concentration, B/U ratios, and age-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ are consistent with pure mechanical mixing of altered oceanic crust (high $\delta^{11}\text{B}$, low B, low B/U, high $^{206}\text{Pb}/^{204}\text{Pb}$; Smith et al., 1995; Hauff et al., 2003) with oceanic sediments (low $\delta^{11}\text{B}$, high B, high B/U, low $^{206}\text{Pb}/^{204}\text{Pb}$; Nakano and Nakamura, 2001; Hauff et al., 2003). Neither LB nor AM mélanges matrix preserve similar mixing trends (not shown), probably reflecting modification by metamorphism.

end-members are consistent with the known composition of AOC and oceanic sediment. Specifically, the component with positive $\delta^{11}\text{B}$, low B concentration, and more radiogenic Pb composition is most likely AOC (Smith et al., 1995; Hauff et al., 2003), while the negative $\delta^{11}\text{B}$, high B concentration, comparatively less radiogenic Pb signature is appropriate for sediments (Nakano and Nakamura, 2001; Hauff et al., 2003). Examination of LB and AM mélanges data in diagrams similar to Fig. 3B–D (not shown) does not result in any covariation for these variables, indicating other metamorphic processes, such as metasomatic fluid flow, overprint any potential mechanical mixing relationships at higher grade conditions.

Our $\delta^{11}\text{B}$ data support previous conclusions regarding up-temperature fluid flow into the amphibolite unit of the Catalina Schist that were previously based upon O isotopic systematics (Bebout, 1991). Fig. 4 illustrates

Rayleigh fractionation models for the $\delta^{11}\text{B}$ evolution of subducted material (Peacock and Hervig, 1999; Benton et al., 2001; Rosner et al., 2003; Bebout and Nakamura, 2003). Although mélanges formation within both the LA and LB mélanges post-dated amphibolite facies metamorphism by at least 10 My, the predicted $\delta^{11}\text{B}$ signature of fluids that would have been devolatilized from these low-grade mélanges at higher temperature (e.g., above chlorite breakdown) agrees well with the observed $\delta^{11}\text{B}$ values within the AM mélanges. Hence we regard the LA and LB mélanges as good proxies for the deep-seated metamorphic source of fluids within the subduction complex. Petrologic distinctions between the more Si- and Al-rich, “crustal” LA and LB mélanges and the strongly ultramafic AM mélanges (Fig. 1) are also congruent with this model, and further support the notion that the mélanges zones of the Catalina Schist are representative of a petrologic structure appropriate for

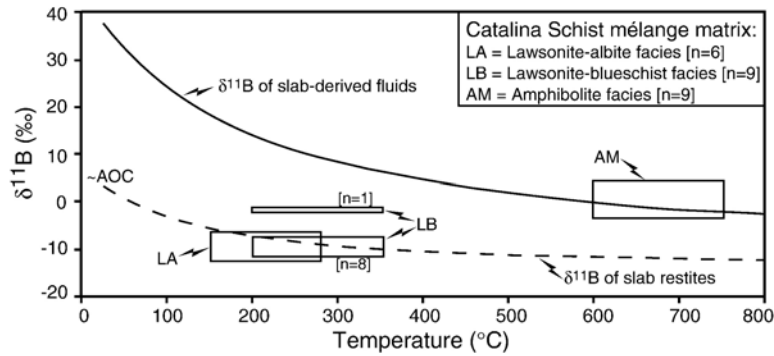


Fig. 4. Evaluation of $\delta^{11}\text{B}$ as a function of metamorphic temperature for the mélange matrix of the Catalina Schist and comparison to existing thermal models for solid/fluid fractionation of $\delta^{11}\text{B}$ during subduction. Temperature-dependent fractionation models for $\delta^{11}\text{B}$ of residual metamorphic solids (i.e., the subducting slab; solid line) and $\delta^{11}\text{B}$ of evolved fluids (i.e., signatures expressed by fluids and arc volcanics; dashed line) are after Peacock and Hervig (1999), Benton et al. (2001), Bebout and Nakamura (2003), and Rosner et al. (2003). LA/LB mélange matrix records $\delta^{11}\text{B}$ consistent with fluid sources of B during subduction, whereas AM mélange records $\delta^{11}\text{B}$ similar to complementary evolved fluids (and arc volcanics). The label “~AOC” marks the approximate $\delta^{11}\text{B}$ of altered oceanic crust ($3.4 \pm 1.1\%$; Smith et al., 1995), for reference.

the slab–mantle interface (Bebout and Barton, 2002; King et al., 2006; cf. Manning, 1995; King et al., 2003). This strongly deformed, metasomatized petrologic system is likely a site of significant mass transfer from the metamorphic environment of the subducting slab to the mantle wedge, and could influence the compositions of “slab-derived fluids” entering the sub-arc region (Bebout and Barton, 2002; Breeding et al., 2004; King et al., 2003; 2006).

5. Pb geochemistry

Within the mélange there is an expectation that Pb should be strongly decoupled from elements such as Ce, Th, and U due to mineral partitioning behavior. Lead is expected to reflect sulfide stability (Chauvel et al., 1995; Kelley et al., 2005), whereas Ce, Th, and U will all likely be controlled by the stability of phosphates, zircon, or epidote-group minerals (Hermann, 2002; Zack et al., 2002; Spandler et al., 2003). Fig. 5 presents variations in Pb/Ce as a function of Pb concentration and U/Th in the mélange sample population. Within LA and LB mélange samples, Pb/Ce correlates positively with Pb (Fig. 5A). We believe that this behavior may record preferential loss of Pb from sulfides, which is supported by Pb isotope geochemistry (below). Variation of U/Th with Pb/Ce (Fig. 5B) for LA and LB mélange samples can be partly explained by mechanical mixing with the observed scatter accounted for by Pb gain and/or U loss mediated by fluid infiltration. Note that the AM mélange samples exhibit distinct behavior compared to lower-grade mélange matrix in that apparent metasomatic addition of U is required.

Measured Pb isotope ratios for mélange matrix from all metamorphic facies of the Catalina Schist (see Online dataset) are both remarkably radiogenic and broadly similar, with no obvious distinction between samples of very different bulk compositions (cf. Fig. 1B). Measured ranges of Pb isotope ratios for all samples are: $^{206}\text{Pb}/^{204}\text{Pb} = 18.740\text{--}22.516$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.628\text{--}15.843$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.388\text{--}44.038$. Measured $^{238}\text{U}/^{204}\text{Pb}$ (μ) and $^{232}\text{Th}/^{204}\text{Pb}$ (ω) ratios display ranges of $\mu = 1.29\text{--}95.80$ and $\omega = 4.70\text{--}640.86$.

In order to illustrate the significance of our measured Pb isotope ratios from the Catalina mélange matrix, we compare the mélange results with reference Pb data from the Izu arc and ODP Site 1149 altered oceanic crust (AOC) and sediments (Hauff et al., 2003) in Fig. 6. Hauff et al. (2003) used Pb isotope data from Site 1149 to constrain the proportional contributions of Pb from the subducting slab that would be required to explain the Pb composition of the Izu arc. Average AOC and sediment compositions were mixed, and the intersection of this mixing line with a regression through the Izu data provides for an identification of the slab contaminant. In this case, Hauff et al. (2003) calculated a mixture of 90–95% AOC/5–10% sediment in the slab signature affecting the Izu arc. This approach is widely applied to volcanic arcs and provides a proportional measure of bulk additions without requiring identification of a specific mass transfer process.

Our mélange data provide an alternative interpretation for the Izu arc data that illustrates the difficulties of applying an approach like that employed by Hauff et al. (2003). Specifically, regression through the Izu arc data intersects the Pb isotope compositions defined by the

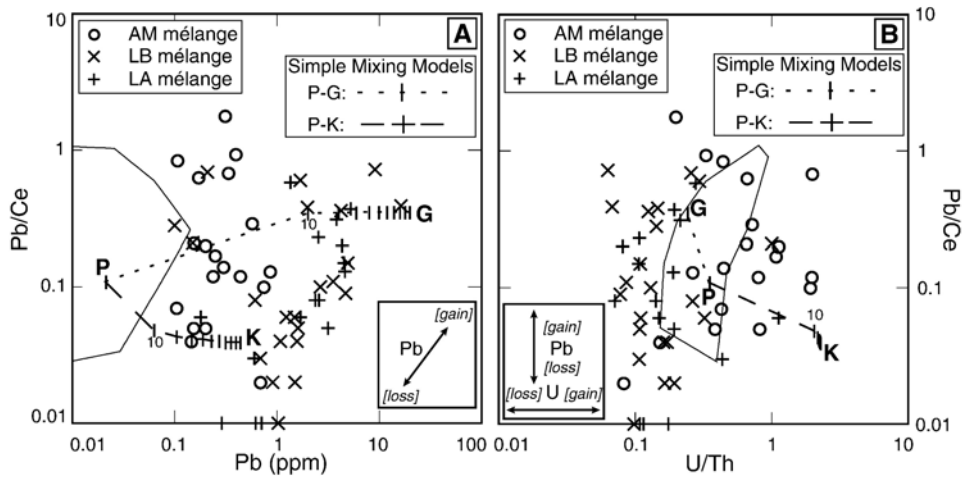


Fig. 5. Variation in Pb/Ce as a function of Pb concentration (panel A, left) and U/Th (panel B, right) for mélange matrix of the Catalina Schist. The open field in both diagrams is the range in variation observed for the Horoman peridotite. Symbols and simple mixing models are identical to Fig. 1B; additionally, inset arrows illustrate vectors for Pb gain/loss (both panels) and U gain/loss (panel B) expected for metasomatic fluid flow. Note that the label indicating the first 10% mixing of GLOSS (G) with peridotite is not shown in panel B, as all increments of mixing are essentially indistinguishable at the scale of presentation.

Catalina mélange in the same fashion as it intersects the AOC/sediment mixing line in the Hauff et al. (2003) model (Fig. 6). To the extent that combined mechanical mixing and metasomatic alteration recorded by the Catalina mélange units represent the slab–mantle interface, it will clearly be very difficult to meaningfully estimate proportions of slab-derived components using an approach that neglects the impact of subduction metamorphism.

The discrepancy between the Catalina Schist mélange Pb isotopic signatures relative to oceanic inputs such as those at Site 1149 could reflect different source characteristics of inputs to the Catalina subduction zone (i.e., more radiogenic trench fill) or, alternatively, fractionation of the U–Th–Pb system during subduction-zone metamorphism. Below, we attempt to reconstruct the signature of continental Pb introduced to the Catalina accretionary complex in an effort to evaluate the possible extent of U–Th–Pb fractionation during subduction metamorphism.

6. Inputs to the Catalina subduction zone

In order to estimate the Pb isotopic composition of continent-derived sediment supplied to the Catalina Schist, we have utilized detrital zircon U–Pb age distributions measured by Grove et al. (in press). Based upon results shown in Fig. 7 and comparable data from the Peninsular Ranges batholith, Grove et al. (in press) concluded that the metasedimentary rocks of the Catalina Schist amphibolite unit were derived from

early Aptian (or older) clastic sediment that was eroded from the Early Cretaceous volcanic rocks and Middle Jurassic–Late Triassic and older flysch wallrocks of the Peninsular Ranges batholith that dominated detritus before the mid-Cretaceous batholith was exposed. Geologic relationships coupled with the abundance of Middle Proterozoic zircon (Fig. 7) indicates that the Pb isotopic signature of the early Aptian (or older) sediment incorporated into the amphibolite unit of the Catalina Schist is best modeled by that of cratonal southwestern North America (Wooden and Miller, 1990; Miller and Wooden, 1994). In contrast, the younger Cenomanian sediment supplied to the lawsonite–blueschist and lawsonite–albite rocks of the Catalina Schist was dominated by plutonic detritus eroded from the western 120–100 Ma zone of the Peninsular Ranges batholith. Accordingly, its Pb isotopic composition was likely similar to that of the western Peninsular Ranges batholith (Kistler et al., 2003).

7. Hypothesized evolution of the U–Th–Pb system

Results from the zircon-based input model for the lawsonite–albite and lawsonite–blueschist facies units of the Catalina Schist (Table 1, Figs. 8 and 9) indicate that local continental sediments are not sufficiently radiogenic to completely explain the Pb isotope composition of the LA and LB mélange matrices. In contrast, the range in input compositions for the amphibolite facies unit (Table 1, Fig. 10) overlaps with the bulk of the measured AM mélange matrix Pb data. Inspection of

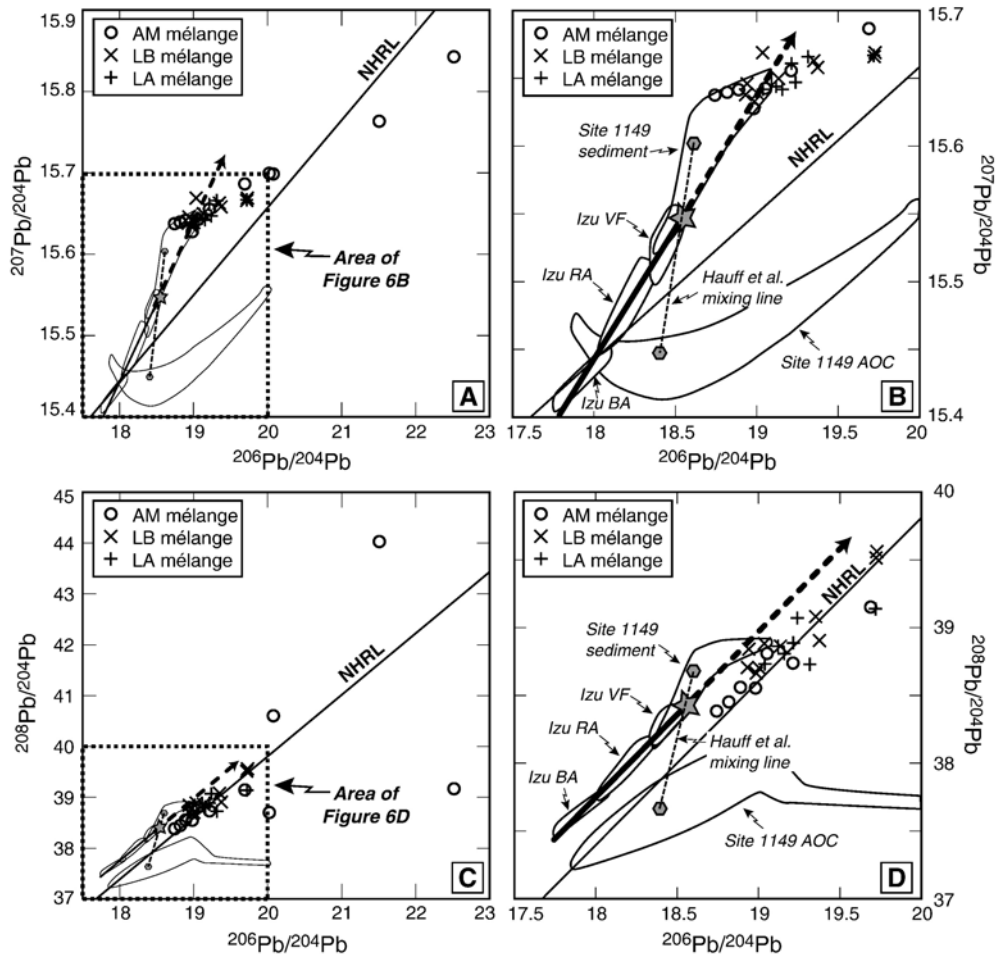


Fig. 6. Pb isotope diagrams comparing the Catalina Schist mélanges matrix to altered oceanic crust (AOC) and sediments from ODP Site 1149 as well as volcanic rocks of the Izu arc; ODP and Izu data are from Hauff et al. (2003). All data shown are present-day ratios. Solid line labeled “NHRL” is the northern hemisphere reference line. Abbreviations used for the Izu data are: VF, volcanic front; RA, rear arc; BA, back arc. Small, gray hexagons are average AOC and sediment compositions, used by Hauff et al. to calculate mixing proportions (thin dotted line, labeled) required to explain a component derived from the subducting Pacific plate (gray star), inferred from a regression through the Izu data (thick solid line). An extension of the Izu regression (thick dashed arrow) indicates a metamorphic mélanges system similar to the Catalina Schist is equally capable of explaining the Izu data.

the results of our input model yields one systematic feature that should be noted prior to a discussion of metamorphic fractionation. For all grades of mélanges, measured $^{207}\text{Pb}/^{204}\text{Pb}$ ratios appear to be more radiogenic than either the $^{206}\text{Pb}/^{204}\text{Pb}$ or $^{208}\text{Pb}/^{204}\text{Pb}$ systems as should be expected for derivation from the constrained input compositions (i.e., continued age correction of $^{207}\text{Pb}/^{204}\text{Pb}$ is consistently more radiogenic than potential inputs). This may reflect either some continental source of Pb with an elevated $^{207}\text{Pb}/^{204}\text{Pb}$ composition that is not considered in our model or a misapproximation of the mean continental sedimentary components derived from available datasets (Wooden and Miller, 1990; Miller and Wooden, 1994; Kistler

et al., 2003), but this shortcoming does not affect our following interpretations.

As is evident in Figs. 8–10, some metamorphic fractionation of the U–Th–Pb system is required to explain the mélanges Pb isotope data. However, this metamorphic fractionation is not immediately apparent. For the U–Pb system, consider that a comparison of measured μ ratios for Catalina mélanges matrix (all samples, 21.39 ± 20.51 [1σ]; range, 1.29–95.80) to the known μ of subduction zone inputs at Site 1149 (15.4 ± 11.0 [1σ]; range, 3.8–31.5; Hauff et al., 2003; see also Kelley et al., 2005) indicates that these two populations are not obviously different, yet the measured mélanges $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios are clearly

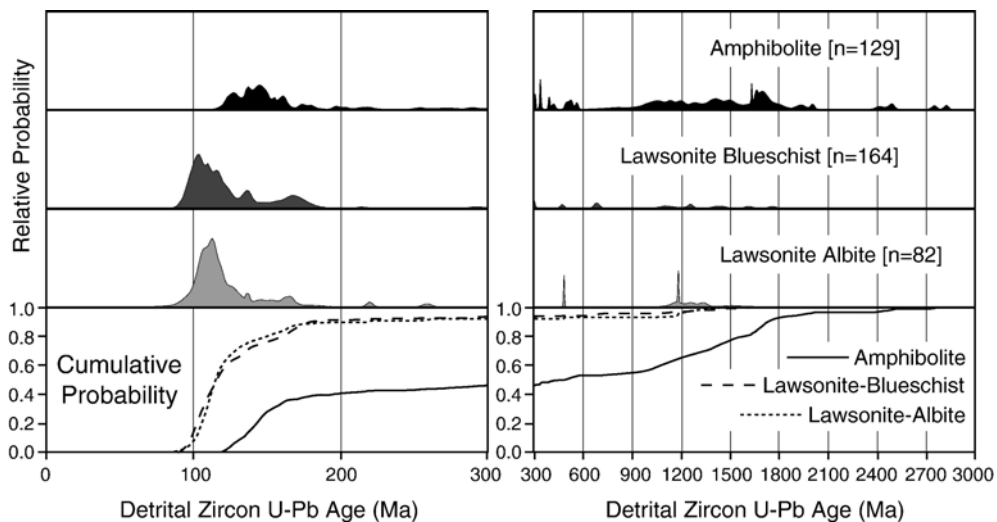


Fig. 7. Detrital zircon U–Pb age spectra for the Catalina Schist; data are from Grove et al. (in press). Proportions of the age spectra were assigned to continental erosional sources to approximate the Pb isotope composition of detritus from California (see Table 1 and subsequent figures).

more radiogenic than prospective inputs and that metamorphic age corrections do not result in Pb ratios predicted by the range of input compositions (Figs. 8–10). Therefore, at some point during metamorphism the uraniumogenic Pb isotope systems must have experienced effective μ ratios higher than at present in order to evolve to their present state.

In contrast, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios do not require significant fractionation in the Th–Pb system, as age correction of $^{208}\text{Pb}/^{204}\text{Pb}$ results in ratios consistent with the range in input compositions. However, many of our samples record ω ratios higher than the 1σ range of inputs measured by Hauff et al. (2003; Site 1149, $\omega = 27.4 \pm 14.0$), suggesting that the Th–Pb system records Pb loss. We will next constrain the possible extent of Pb loss from the mélangé during metamorphism from Th–Pb, but it is only reasonable to apply this exercise to samples of LA and LB mélangés, as available evidence suggests that the AM mélangé is not representative of a subducted input (Grove et al., in press), but rather represents the deformed and metasomatized edge of the mantle wedge (see above $\delta^{11}\text{B}$ data; Bebout and Barton, 2002; King et al., 2006).

We estimated Pb loss from samples of LA and LB mélangé matrices where $\omega \geq 42$ (13 of 17 samples), because these record higher ω than is typical of subduction zone inputs (Hauff et al., 2003). When Pb loss is calculated using the baseline $\omega = 27.4$ of Hauff et al. (2003), LA/LB mélangé matrix records Pb loss ranging from 30 to almost 99%. These are very broad estimates due to the range in ω , but more importantly are imprecise because unconstrained protolith compositions of

mélange matrix samples reflect the complexities of their petrogenesis. However, this magnitude of Pb loss is reasonable to explain differences between age-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ and constrained input compositions. Trajectories illustrating the calculated synmetamorphic in-growth of radiogenic Pb due to Pb loss are shown in Figs. 8–10 for periods of 0.5, 1, and 2 Ma; these time spans are appropriate for typical subduction rates and the known period of <2–4 Ma between deposition and peak metamorphism experienced by the Catalina Schist (Grove et al., in press).

This Pb-loss scenario may explain the data, but the point still stands that measured μ ratios are not distinguishable from oceanic inputs. Therefore, while Pb loss appears to have produced elevated μ , this interpretation further requires this to be a transient metamorphic stage, followed by later U loss. Although convoluted in requiring separate Pb- and U-loss events to produce μ ratios consistent with oceanic inputs, this interpretation could reflect a plausible history of mineral reactions occurring during subduction. Our preferred interpretation is that Pb loss occurs during early metamorphism via desulfidation reactions, as has been proposed previously to occur during subduction (Chauvel et al., 1995; Kelley et al., 2005). Early subduction desulfidation is probably also recorded by elevated sulfate concentrations emanating from forearc serpentinite seamount springs (Mottl et al., 2004). Such reactions will create a transient state of a few million years in which μ is elevated to a degree sufficient to explain the gap between input compositions and the age-corrected mélangé $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ data (Figs. 8–10). Subsequent U loss could

Table 1
Model estimate of erosional sources of continental Pb to the Catalina subduction zone

Western Peninsular Ranges Batholith (Kistler et al., 2003)			
Age bin	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
98–105 Ma	19.005	15.631	38.741
105–109 Ma	19.095	15.623	38.728
113–117 Ma	18.852	15.593	38.388
119–125 Ma	19.091	15.623	38.806

Mojave Terrane (Miller and Wooden, 1994)			
Age bin	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
145 Ma total mean	18.16	15.57	39.04
160 Ma mean	17.39	15.51	39.34

Sonora Terrane (Wooden and Miller, 1990)			
Age bin	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
Proterozoic	20.69	15.77	38.98

Distribution of detrital zircon U–Pb age spectra assigned to erosional sources of continental Pb

	Lawsonite–albite facies	Lawsonite–blueschist facies	Amphibolite facies
Maximum depositional age	98±3 Ma	98±3 Ma	121±2 Ma
WPRB 98–105 Ma	12.49%	21.56%	n/a
WPRB 105–109 Ma	22.23%	16.74%	n/a
WPRB 113–117 Ma	20.76%	13.67%	n/a
WPRB 119–125 Ma	10.74%	8.99%	5.04%
Mojave 145 Ma	5.79%	7.30%	15.31%
Mojave 160 Ma	7.84%	9.68%	8.97%
Sonora Proterozoic	6.77%	3.63%	47.54%
Sum of variance	86.61%	81.58%	76.85%

Model results			
	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
LA California	18.931	15.615	38.754
LB California	18.815	15.608	38.795
AM California	19.698	15.691	39.024

Notes: All Pb ratios modeled in this study are measured ratios. Pb concentrations were not available for the Mojave terrane, so mixing calculations are for proportionate mixing of isotope ratios only. Model results were normalized to 100% total variance.

occur in several ways, either when metamorphic reactions consume U-host minerals, when U hosts may be destabilized within mélangé matrix by modification of activity ratios buffered by mélangé matrix bulk composition (Bebout and Barton, 2002; Breeding et al., 2004; King et al., 2006), or preferential fractionation of U from Th by incongruent dissolution of minerals such as apatite or epidote to form monazite or allanite, respectively (cf. Antignano and Manning, 2004). Although both Pb and U loss are unlikely to occur at similar magnitudes, competing reaction pathways occurring within the subducting

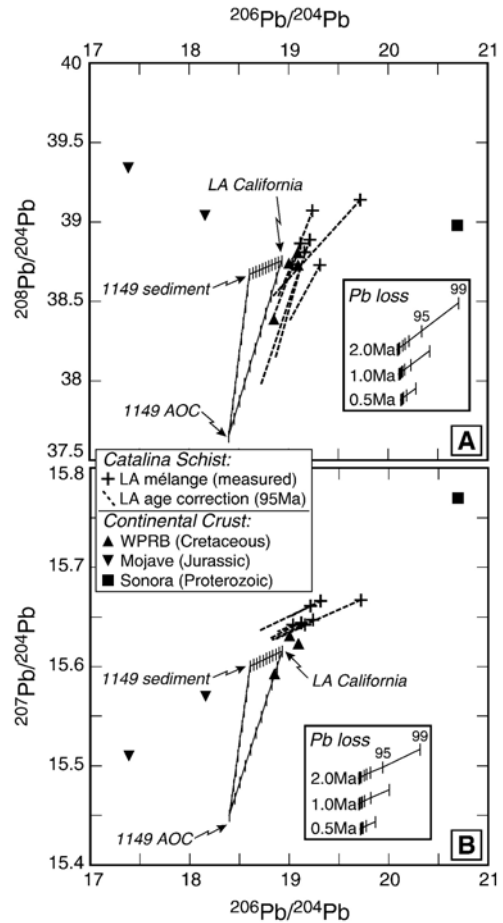


Fig. 8. Pb isotope diagrams constraining the likely compositional range of Pb input to the Catalina subduction zone for lawsonite–albite facies mélangé matrix of the Catalina Schist. Solid lines with ticks (10% increments) are for mixing of input end-members; only isotope ratios were mixed, so the mixing lines are not proportional for end-member concentrations. End members used in mixing calculations are the altered oceanic crust and sediments from ODP Site 1149 (Hauff et al., 2003) and the detrital zircon-based continental composition for the lawsonite–albite facies calculated in Table 1 (“LA California”). Reference compositions for the western Peninsular Ranges Batholith (WPRB) and the Mojave and Sonora terranes are shown by filled symbols. All data shown are present-day ratios; dotted lines represent metamorphic age corrections for the LA mélangé matrix. Inset boxes in both panels illustrate the magnitude of additional radiogenic Pb ingrowth due to Pb loss and elevated μ and ω for time scales of 0.5, 1, and 2 Ma; these growth curves are labeled for 95% and 99% Pb loss only to clarify the diagram.

section may act to create μ ratios apparent within the mélangé data that are similar to sea-floor inputs to subduction zones. Similar mobility of these elements has been demonstrated in high-pressure metamorphic fluids interacting with eclogites and metasomatized metabasites (John et al., 2004; Saha et al., 2005), in some cases resulting in similar fractionated Pb isotope signatures (Usui et al., 2006).

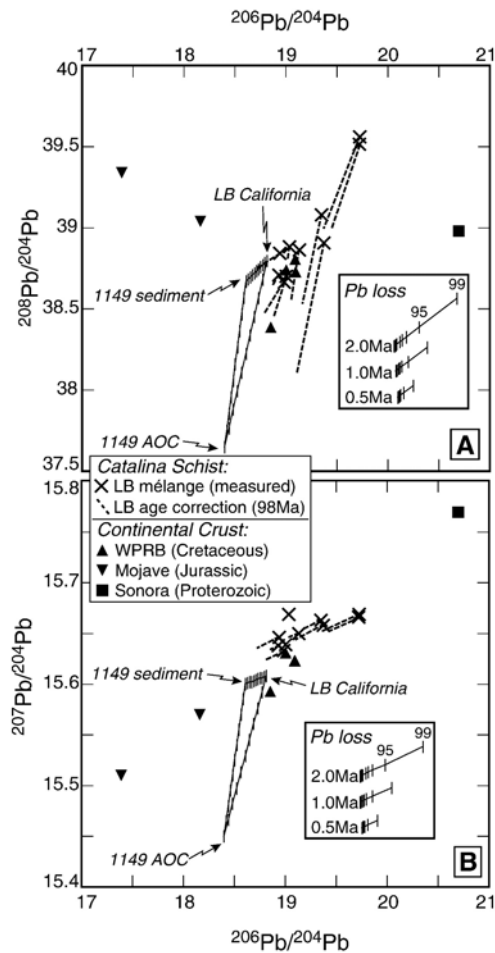


Fig. 9. Pb isotope diagrams constraining the likely compositional range of Pb input to the Catalina subduction zone for lawsonite–blueschist facies mélangé matrix of the Catalina Schist. Solid lines with ticks (10% increments) are for mixing of input end-members; only isotope ratios were mixed, so the mixing lines are not proportional for end-member concentrations. End members used in mixing calculations are the altered oceanic crust and sediments from ODP Site 1149 (Hauff et al., 2003) and the detrital zircon-based continental composition for the lawsonite–blueschist facies calculated in Table 1 (“LB California”). Reference compositions for the western Peninsular Ranges Batholith (WPRB) and the Mojave and Sonora terranes are shown by filled symbols. All data shown are present-day ratios; dotted lines represent metamorphic age corrections for the LB mélangé matrix. Inset boxes in both panels illustrate the magnitude of additional radiogenic Pb ingrowth due to Pb loss and elevated μ and ω for time scales of 0.5, 1, and 2 Ma; these growth curves are labeled for 95% and 99% Pb loss only to clarify the diagram.

Assigning a specific genetic process for the AM mélangé Pb data is problematic. In one scenario, our $\delta^{11}\text{B}$ data (Fig. 4) and other stable isotope evidence (Bebout, 1991, 1997) suggest that Pb isotope signatures of the AM mélangé are better viewed as a record of the Pb composition of evolved fluids likely derived from

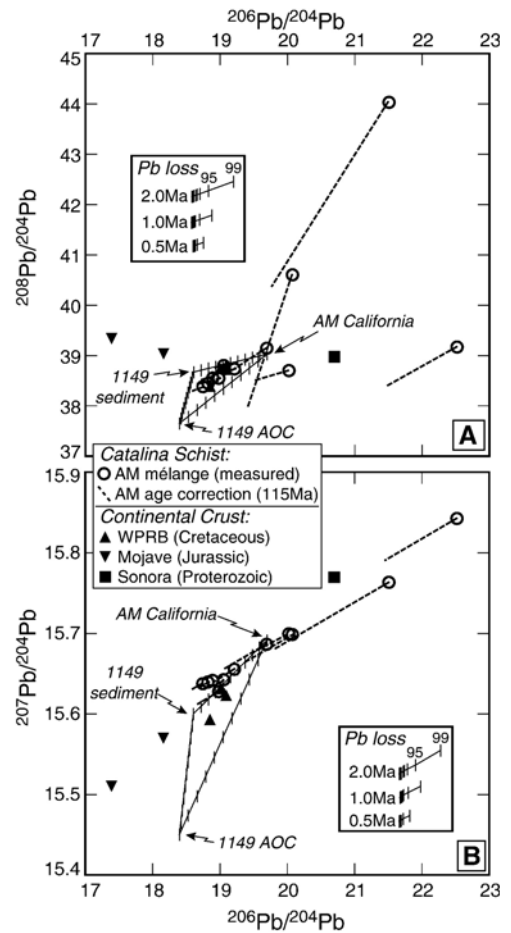


Fig. 10. Pb isotope diagrams constraining the likely compositional range of Pb input to the Catalina subduction zone for amphibolite facies mélangé matrix of the Catalina Schist. Solid lines with ticks (10% increments) are for mixing of input end-members; only isotope ratios were mixed, so the mixing lines are not proportional for end-member concentrations. End members used in mixing calculations are the altered oceanic crust and sediments from ODP Site 1149 (Hauff et al., 2003) and the detrital zircon-based continental composition for the amphibolite facies calculated in Table 1 (“AM California”). Reference compositions for the western Peninsular Ranges Batholith (WPRB) and the Mojave and Sonora terranes are shown by filled symbols. All data shown are present-day ratios; dotted lines represent metamorphic age corrections for the AM mélangé matrix. Inset boxes in both panels illustrate the magnitude of additional radiogenic Pb ingrowth due to Pb loss and elevated μ and ω for time scales of 0.5, 1, and 2 Ma; these growth curves are labeled for 95% and 99% Pb loss only to clarify the diagram.

underlying, lower-T and largely metasedimentary parts of the subduction zone. However, while most of the AM mélangé Pb data are indistinguishable from the LA/LB mélangé, the AM mélangé data are also similar to the likely input compositions calculated for the amphibolite unit and the signature of the western Peninsular Ranges Batholith (the coeval igneous suite associated with the

Catalina Schist; Figs. 8–10; Kistler et al., 2003). As such, it is equally plausible that the Pb isotope composition of the AM mélange may simply record retention of protolith Pb within the amphibolite unit during metamorphism rather than transfer of Pb from lower-grade mélange to the Peninsular Ranges Batholith magma source region. Either model is compatible with the available data, so that distinguishing control of the AM mélange Pb systematics via internal protolith composition versus an externally derived infiltrating fluid is difficult to distinguish with our available data.

Although the majority of the AM mélange Pb data resemble those for the lower-grade mélange (Fig. 6), 5 of the 11 AM mélange samples preserve Pb compositions more radiogenic than the lower-grade mélange (Figs. 6, 8–10) and are, in general, associated with greater extremes in μ and ω . These features of the data suggest that some metasomatic agents within subduction zones may transfer extreme Pb isotope compositions. These heterogeneities probably reflect the association of both fluid- and melt-related metasomatism within the AM mélange (Sorensen and Barton, 1987; Sorensen and Grossman, 1989; Bebout and Barton, 1989, 1993), likely resulting in distinct signatures. Therefore, one interpretation is that samples of the AM mélange recording Pb signatures similar to the LA/LB mélange represent a hydrous fluid that mobilized Pb with little U and Th, whereas the more radiogenic AM samples record the influence of melts that mobilized significant U and Th in addition to Pb.

8. Possible significance of mélange B–Pb signatures for arc volcanism

To further evaluate whether the B–Pb isotope signature of the Catalina Schist mélange matrix is an appropriate record of evolved fluids from a heterogeneous subducting section, we have compared these inferred fluids to several modern volcanic arcs (Izu; Ishikawa and Nakamura, 1994; Mariana, Ishikawa and Tera, 1999; Central Andes, Rosner et al., 2003; northeastern Japan; Moriguti et al., 2004). Fig. 11 presents this experiment, where B–Pb isotope signatures of metamorphic fluids associated with the Catalina mélange matrix are mixed with a depleted mantle component used to approximate the mantle wedge. Fig. 11 considers mixing of two fluids with the mantle wedge. Both fluid mixing end-members have an identical $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic composition of 19.0, while the $\delta^{11}\text{B}$ of the fluid end-members evolves from a low-temperature composition appropriate for the blueschist facies of +10.0‰ to a high-temperature $\delta^{11}\text{B}$ of -3.0‰ . Synmetamorphic fractionation of Pb isotope ratios is not considered in the

model for the sake of simplicity, although this fractionation is certainly plausible. Mixing lines between fluids and the mantle wedge used in Fig. 11 should not be considered inherently diagnostic for any of these subduction systems, but primarily serve to guide the reader to mixing patterns expressed by different B/Pb ratios.

Using Fig. 11 as a guideline, we examine how B–Pb isotope data for these four arcs may reflect the derivation of “slab” signatures from sub-arc mélange. All of the arc data are consistent with derivation of subducted B–Pb from mélange-equilibrated fluids, while trends of decreasing $\delta^{11}\text{B}$ and progressively lower B/Pb ratios suggest Rayleigh fractionation of B during metamorphism is the dominant control on B evolution during subduction.

Two temperature-dependent factors probably dominate the observed $\delta^{11}\text{B}$ signatures of the Izu and Mariana arcs. Foremost, the “colder” subduction typical of these arcs will yield fluids with more enriched $\delta^{11}\text{B}$ (cf. Fig. 4; Peacock and Hervig, 1999; Benton et al., 2001; Bebout and Nakamura, 2003; Rosner et al., 2003), while colder temperatures will also favor retention of phengitic white mica to greater depths, which will also act to maintain higher $\delta^{11}\text{B}$ of fluids buffered by the

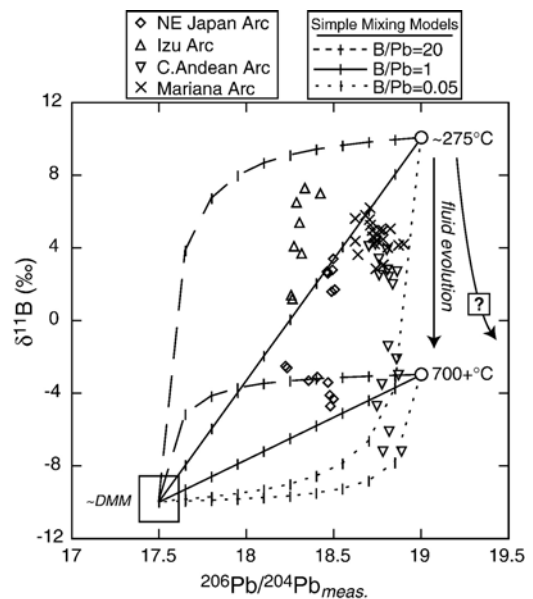


Fig. 11. Comparison of B–Pb isotope systematics for fluids derived from the Catalina Schist mélange matrix to volcanic rocks of four modern arcs (Izu, Ishikawa and Nakamura, 1994; Mariana, Ishikawa and Tera, 1999; Central Andes, Rosner et al., 2003; northeastern Japan, Moriguti et al., 2004). Simple mixing between mélange fluid compositions and a depleted mantle composition at varying B/Pb ratios is capable of reproducing these arc compositions, suggesting derivation of fluids from metamorphic mélange matrix in active subduction zones is a reasonable alternative model. See Section 8 for a full discussion of each arc.

metamorphic system (Marschall et al., 2007-this issue). These factors controlling fluid $\delta^{11}\text{B}$ can readily explain observed $\delta^{11}\text{B}$ for the Izu and Mariana arcs.

The across arc decline in $\delta^{11}\text{B}$ observed for Izu was interpreted by Ishikawa and Nakamura (1994) to represent different degrees of mixing between a relatively constant $\delta^{11}\text{B}$ slab component with the mantle, but another explanation might be that the decline reflects progressive Rayleigh fractionation of $\delta^{11}\text{B}$ as a function of temperature combined with progressively lower B/Pb ratios expressed by metasomatic fluids due to this devolatilization. For the Mariana system, Ishikawa and Tera (1999) inferred two distinct fluids affecting the mantle. One fluid was very homogenous in composition, whereas heterogeneity in B isotopes expressed in some volcanic centers was interpreted as a distinct fluid influenced by localized subducting seamounts. This Mariana dataset reflects along-arc sampling, so variations in $\delta^{11}\text{B}$ are not likely attributable to thermal structure of the metamorphic system. Our interpretation of the Mariana data is very similar to Ishikawa and Tera (1999), only different in that our data and other recent studies allow for a theory directly relating the two fluids to mineralogic variations in the metamorphic system. The first, homogenous fluid must represent the dominant mélange matrix at depth, in which mélange bulk composition primarily reflects mixing between AOC and pelagic sediments of the Pacific plate and is broadly consistent along arc strike. Therefore, variations in volcanic $\delta^{11}\text{B}$ for centers sampling the homogenous fluid probably only reflect modulated B/Pb ratios of evolved fluids originating from small differences in mineral modes. The heterogeneous second fluid type has higher observed $\delta^{11}\text{B}$, so these variations probably reflect zones of mélange enriched in K over the dominant Mariana mélange, stabilizing higher modal phengite, allowing for comparatively greater retention of ^{11}B than normal (Marschall et al., 2007-this issue), and thereby buffering the anomalous fluid composition.

Our alternative interpretation for the northeastern Japan data in Fig. 11 differs from Moriguti et al. (2004) principally in inferring a different residual solid buffering fluid compositions derived from the metamorphic system. Moriguti et al. (2004) compared phase equilibria for subducting hydrous MORB relative to depth-to-slab of the NE Japan volcanoes and concluded that variations in $\delta^{11}\text{B}$ originated from decomposition of B-bearing minerals such as tourmaline rather than fluids predicted by Rayleigh-type fractionation models due to a mismatch between expected fluid and observed volcanic $\delta^{11}\text{B}$. However, variations in modal phengite will act to modulate initial conditions of Rayleigh-type

models (Marschall et al., 2007-this issue) and modal phengite in any mélange metamorphic system will further depend upon the activity ratios buffered by mélange bulk chemistry (Bebout and Barton, 2002; Breeding et al., 2004; King et al., 2006). The across-arc variation observed in NE Japan follows decreasing $\delta^{11}\text{B}$ and B/Pb ratios with increasing depth-to-slab; in Fig. 11 the high $\delta^{11}\text{B}$ group has B/Pb ~ 2 –5, whereas in the low $\delta^{11}\text{B}$ group B/Pb is more typically < 2 . This pattern of decreasing $\delta^{11}\text{B}$ concurrent with a lower relative influence of metamorphic B is consistent with progressive loss of B by Rayleigh fractionation of metamorphic mélange within the subduction zone.

Our analysis of the Central Andean data strongly supports the conclusions of Rosner et al. (2003), consistent with simple progressive B loss during thermal evolution of the subducting slab. The Central Andean data broadly define decreasing $\delta^{11}\text{B}$ as a function of depth-to-slab and therefore increasing metamorphic temperature (cf. Fig. 4; Peacock and Hervig, 1999; Benton et al., 2001; Bebout and Nakamura, 2003; Rosner et al., 2003). When Pb isotope data are integrated to the comparison (Fig. 11), note that the low-temperature group with enriched $\delta^{11}\text{B}$ favors interpretation of a B/Pb ratio > 1 for the metamorphic fluid, whereas the high-temperature, depleted $\delta^{11}\text{B}$ group suggests the influence of a fluid with B/Pb < 1 . Therefore, the Andean data strongly support models where progressive B loss and concurrent Rayleigh fractionation of $\delta^{11}\text{B}$ during metamorphism control the signature of arcs.

However, we must stress that the apparent agreement between fluid compositions predicted by Rayleigh-type models and the Andean data may simply reflect the use of the Andean data to constrain boundary conditions for Rayleigh calculations. It is extremely likely that across-arc variations in temperature-sensitive tracers such as $\delta^{11}\text{B}$ that are also strongly sensitive to phase equilibria may be unique between, or even within, individual subduction systems due to the poorly-defined petrology of the sub-arc metamorphic system. The influence of variables such as initial sediment/basaltic input, styles of mechanical/metasomatic mixing, and prograde metamorphic path may develop significant petrochemical distinctions in the sub-arc mélange dominating any particular margin. Therefore, until processes governing the metamorphic system are constrained further, we consider it inherently dangerous to assume that signatures of mass transfer such as $\delta^{11}\text{B}$ will be expressed in a consistent manner for all subduction zones.

The overall success of the experiment in simulating arc B–Pb isotope signatures is compelling in that the

choice of mobilized fluid signals recorded by mélange matrix as the source of a contaminant further incorporates a diverse number of metamorphic, metasomatic, and deformational processes that surely occur during subduction, but are not widely considered in petrologic models for slab-to-arc mass transfer. Our impetus to explore the role of mélange matrix as the petrologic reservoir actively influencing fluid chemistry during subduction reflects a developing preponderance of evidence indicating that measurable geochemical anomalies related to fluid flow occur within structures such as mélange or fractures (Bebout and Barton, 2002; Breeding et al., 2004; John et al., 2004; King et al., 2006; Ague, 2007-this volume; Zack and John, 2007-this volume) rather than more “coherent” lithologies such as tracts of UHP eclogite (e.g., Chalot-Prat et al., 2003; Spandler et al., 2003, 2004; Spandler and Hermann, 2006). While coherent examples of UHP rock that can be directly correlated with pre-subduction inputs must certainly contribute to overall fluid production during subduction, the collation of fluids, melts, or other mobile agents within high permeability pathways such as mélange matrix indicate that fractionation and partitioning between evolved mobile phases and the solid rock of these pathways will exert a stronger control on the geochemical signature of metasomatic agents than original sources (cf. Ague, 2007-this volume; Bebout, in press; Zack and John, 2007-this volume).

9. Conclusions

Within the Catalina Schist, mélange matrix consists of hybridized rock compositions formed from peridotite, basalt, and sediment protoliths via fluid and mechanical metasomatic mixing vectors. While B and Pb concentrations mimic trends expected for mechanical mixing, isotope ratios for these elements are hybridized and fractionated during metamorphism. Using our new B and Pb isotope measurements in conjunction with detrital zircon ages, we have demonstrated the following:

1. At low-grade, lawsonite–albite conditions B systematics appear to be dominated by mechanical exchange, but fluid-related homogenization of the B system becomes more important at only modestly higher-temperature lawsonite–blueschist conditions. Boron isotope compositions of amphibolite facies mélange require B in this unit to be derived from an external source, an interpretation consistent with previous stable isotope study of the same mélange unit.
2. Comparison of the B isotope data to proposed temperature-dependent Rayleigh fractionation models for the evolution of $\delta^{11}\text{B}$ within subduction zones indicate lawsonite–albite and lawsonite–blueschist mélange matrices are appropriate sources of B derived from subducting lithosphere, while amphibolite mélange records $\delta^{11}\text{B}$ similar to the composition of evolved fluids affecting arc magmas. The B isotope results are compatible with the previously presented model for sources and transport of fluid within the Catalina Schist subduction zone based on O and H isotope data: $\delta^{11}\text{B}$ values for the amphibolite facies mélange matrix are consistent with infiltration by B-bearing fluid produced in lower-T metasediment-rich domains, whereas the lower-grade lawsonite–albite and lawsonite–blueschist tectonometamorphic units represent possible analogs for the sources of this B-bearing fluid.
3. Pb isotope ratios for all grades of mélange matrix are broadly similar, despite significant differences in bulk-rock composition. Comparison of the mélange matrix Pb ratios to the modern Izu arc indicates that a metamorphic mélange system within active subduction zones could deliver Pb compositions to the mantle wedge appropriate for a slab component.
4. Using detrital zircon age spectra for the Catalina Schist, we have approximated the probable composition of continental detritus input to the Catalina subduction zone. Our estimates of input Pb compositions using these data, in conjunction with the composition of altered oceanic crust and oceanic sediments, indicate that inputs for the lawsonite–albite and lawsonite–blueschist facies units are insufficiently radiogenic to explain the Pb composition of their mélange matrix, requiring metamorphic fractionation within the U–Th–Pb system during subduction. Modeled inputs for the amphibolite facies unit are more radiogenic and agree with measured ratios, suggesting measured Pb compositions may reflect efficient retention of protolith Pb during amphibolite mélange formation. However, the strong similarity of the amphibolite Pb data to the lower-grade units and the coeval Peninsular Range magmatic suite preclude simple genetic interpretations of the amphibolite Pb data.
5. Assuming that sedimentary inputs are adequately represented, the U–Th–Pb systematics for lawsonite–albite and lawsonite–blueschist mélange samples appear to require a two-stage fractionation history, where Pb is lost early during metamorphism due to desulfidation reactions, followed by U loss. This transient, 1–2 m.y. stage of elevated μ is

sufficient to explain gaps between age-corrected Pb ratios and constrained input compositions. Th does not appear to be significantly mobilized during metamorphism.

- Theoretical mixing of inferred fluid B–Pb isotope signatures from the Catalina Schist mélange matrix with mantle compositions can reliably reproduce the composition of arc volcanics. The simplicity of the model in explaining existing arc data is extremely compelling in that the model implicitly introduces a large number of additional variables to the overall system, yet explains anomalous arc compositions with ease. We suggest that geochemical signatures associated with “slab” additions to arcs probably reflect the influence of mélange zones, as mobile metasomatic agents such as fluids, melts, or miscible super-critical species should be concentrated within these high-permeability pathways consisting of hybridized lithologies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2007.01.009](https://doi.org/10.1016/j.chemgeo.2007.01.009).

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