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# Metamorphic chemical geodynamics of subduction zones

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## Abstract

Study of metamorphic suites directly representing the deep subduction of altered oceanic crust and sediments can help elucidate the geochemical evolution of the forearc-to-subarc slab–mantle interface, the nature of slab-derived fluids added to arc lava source regions, and the chemical changes in subducting rocks potentially contributing to the geochemical heterogeneity of the deeper mantle. The stage is set for more focused geochemical study of high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic suites incorporating knowledge of mineral chemistry and reactions, kinetics and disequilibrium, prograde and exhumation-related  $P$ – $T$  paths, fluid flow and fluid–rock interactions, and experimental evidence for the physical and chemical properties of fluids at the pressures and temperatures experienced by subducting slabs. Detailed studies of HP and UHP metamorphism published thus far provide some insight regarding the geochemical effects of devolatilization and the element transport capabilities of metamorphic fluids in forearc regions of subduction zones (<100 km). Future research in this rapidly developing field should prioritize study of UHP suites metamorphosed at depths >100 km, which have potentially experienced partial melting, with the goal of better characterizing fluid additions to arcs from subducting slabs and sediments and the compositions of dehydration and melting residues that could impact geochemical compositions of the mantle including source regions for ocean island basalts.

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## 1. Introduction

High-pressure (HP) and ultrahigh-pressure (UHP) metamorphic suites that experienced pressure–temperature ( $P$ – $T$ ) conditions similar to those thought to occur deep in modern subduction zones (Stern, 2002; Carswell and Compagnoni, 2003) would seem to present a chemical and isotopic treasure trove of testable hypotheses bearing on the geochemical evolution of arc lavas (Elliott, 2003; Tatsumi, 2005), the direct igneous products of subduction, and contributions of subducted materials to chemical/isotopic heterogeneity in deeper parts of the mantle (Hofmann,

2003; McKenzie et al., 2004; Fig. 1). In the best case, these metamorphic suites, which contain sedimentary and igneous lithologies with appropriate seafloor protoliths, directly reflect geochemical evolution at/near the slab–mantle interface and can help us further characterize slab processes only inferred in the many geochemical studies of arc lavas and ocean island basalts (OIB). Thus, the field of “metamorphic chemical geodynamics” (after Allègre, 1982; Zindler and Hart, 1986) comprises characterizing the geochemical changes in deeply subducted lithologies and determining the roles of various types of fluids in element transfer at depth in subduction zones.

In general, the seafloor sediments and altered oceanic basalts subducting into modern convergent margins are

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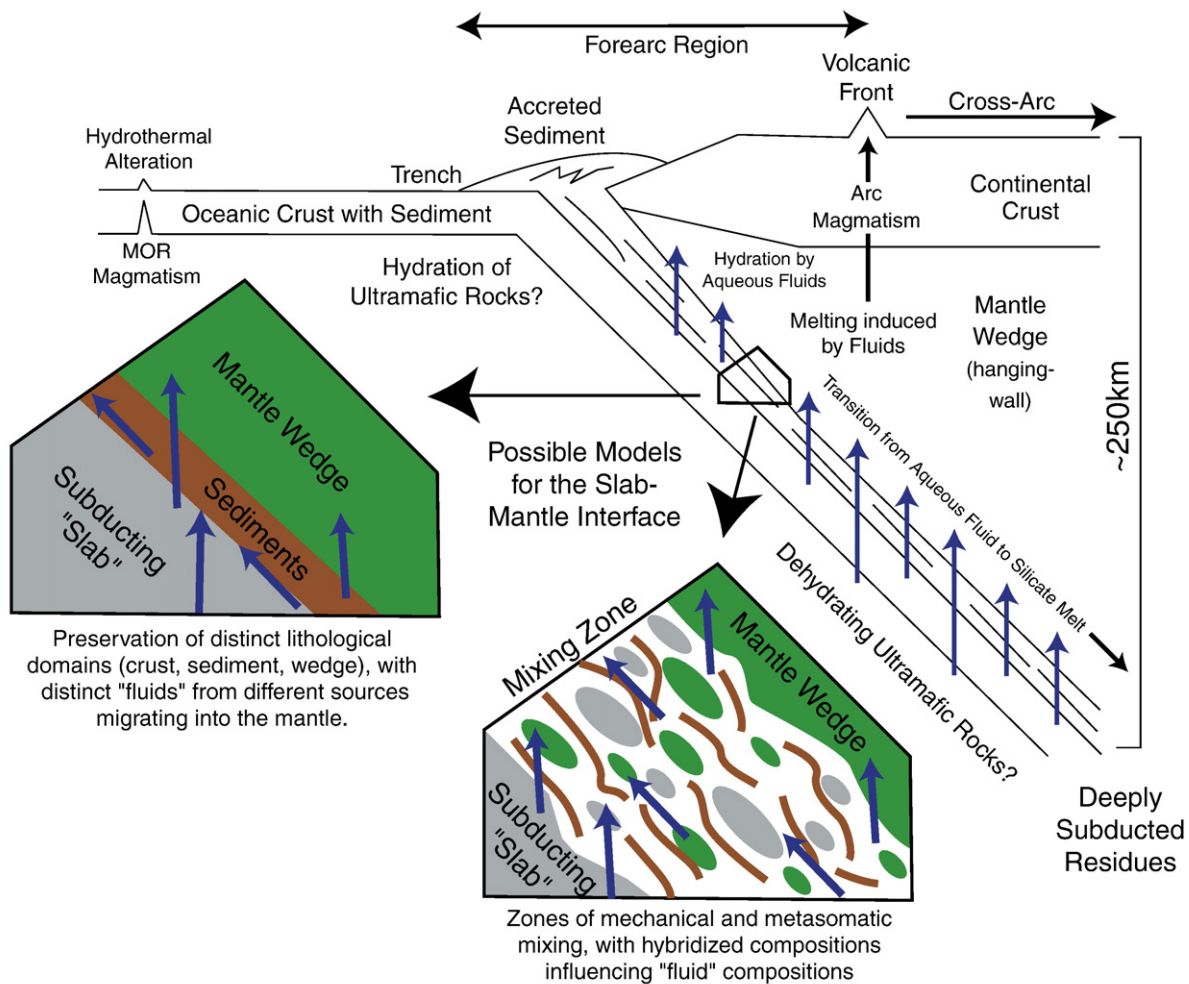


Fig. 1. Sketch of an ocean–continent subduction zone, illustrating key structural elements, some selected flux pathways, areas of remaining uncertainty in considerations of subduction-zone recycling, and two models for the nature of the slab–mantle interface (Stern, 2002; see text for discussion). Oceanic crust (and its associated mantle part of the oceanic lithosphere), variably altered geochemically at mid-ocean ridges (MOR), and sediment deposited onto this crust, are deeply subducted, contributing fluids and elements to the mantle wedge (hanging wall). It is possible that fluids are also contributed from the ultramafic part of the subducting oceanic lithosphere previously hydrated during slab bending in trench regions. On this figure (insets and main figure), the blue arrows indicate additions of slab-derived “fluids” to the mantle wedge. At shallower levels (forearc regions, in particular), these fluids are thought to be aqueous fluids, whereas the fluids added to the mantle wedge at greater depths (beneath volcanic arcs and into the deeper mantle) likely transition into being silicate melts.

enriched in the same chemical species thought to be enriched in subduction-related lavas by fluids released by subducting rocks and ascending into the mantle wedge (e.g., Rb, Cs, Ba, B, and Li, in addition to Th, U, Pb,  $^{10}\text{Be}$ , and the LREE; (see Elliott, 2003; Morris and Ryan, 2003; Tatsumi, 2005; see Fig. 2). Attempts to quantify this slab-to-mantle chemical flux rely on a modest number of experimental studies investigating the partitioning of these and other elements among minerals and various types of fluid (alkali-chloride aqueous fluids, hydrous silicate melts, and transitional supercritical liquids (Manning, 2004; Kessel et al., 2005a,b; Hermann et al.,

2006). Although it appears that aqueous fluids are the dominant fluid type released by subducting sediment and basalt in forearc regions (Hermann et al., 2006; see Fig. 1), the supercritical liquids and hydrous silicate melts may be more important beneath volcanic fronts and across arcs (e.g., for transporting Be, Th; Elliott, 2003; Morris and Ryan, 2003). Many geochemical studies of OIB invoke the presence, in mantle source regions, of subducted slabs chemically modified by metamorphism (e.g., loss of Pb and U; Hart and Staudigel, 1989; Chauvel et al., 1995; Bach et al., 2003; Kelley et al., 2005). In this paper, I discuss recently published field and geochemical

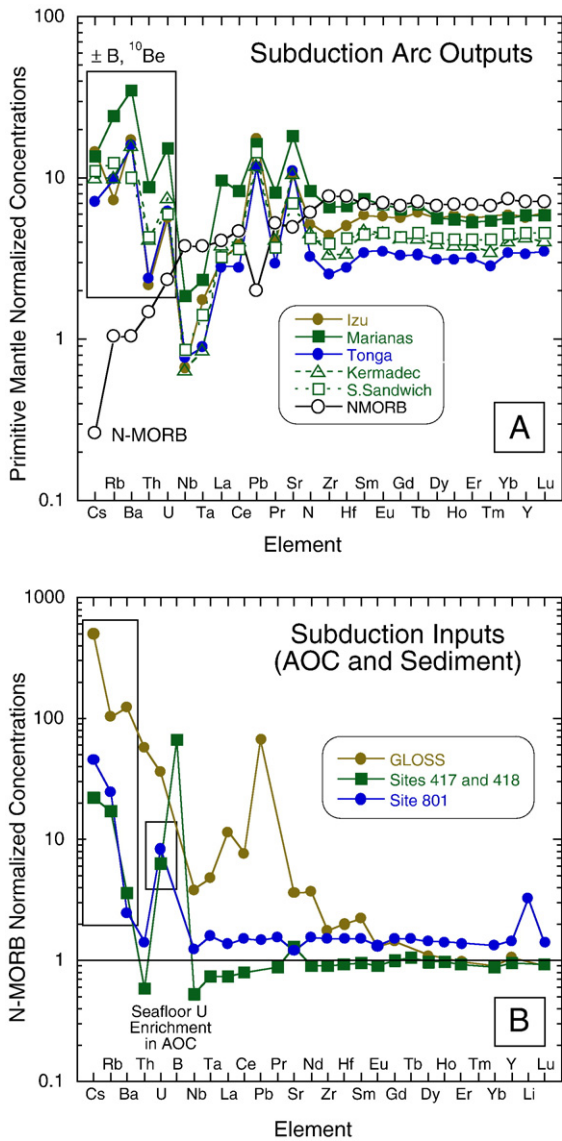


Fig. 2. The arc outputs (A) and AOC and sediment inputs (B) of subduction-zone cycling, showing the inheritance of non-magmatic trace element signatures in seafloor basalt related to interactions with seawater, and the GLOSS (globally subducting sediment) composite from Plank and Langmuir (1998). Data are normalized to primitive mantle or N-MORB, both from Hofmann (1988), and elements are in order of increasing incompatibility (tendency to partition into melts) to the left during mantle melting. Data for AOC are from Staudigel (2003), Kelley et al. (2003). The boxes on (A) and (B) indicate elements that are enriched in both arc volcanic rocks (outputs of subduction) and seafloor sediments and basalts (inputs of subduction). Transfer of the elements enriched in subducting materials to the mantle wedge depends on the relative partitioning of the elements into fluids during fluid release from the slab.

observations from study of HP and UHP metamorphic suites that are relevant to considerations of slab-to-mantle element transfer and chemical change in deeply subduct-

ing rocks, and I highlight some particularly promising avenues for future research on HP and UHP metamorphic suites aimed at this set of problems.

## 2. Nature of the slab–mantle interface

It is first worth considering the makeup of the package of rocks being subducted into Earth's subduction zones. The interface between the subducting slab and the overlying mantle wedge is generally thought to be composed of heterogeneously deformed oceanic crust and sedimentary cover juxtaposed with variably hydrated and metasomatized hanging-wall ultramafic rocks (see the sketches in Fig. 1). In some forearcs, processes of sediment accretion and underplating can result in the offscraping of the upper part of the sediment section, thus preventing its deep subduction (see Fig. 1). In other subduction zones, materials from the forearc hanging wall are incorporated into the subducting package of rocks, resulting in their “erosion” and possible deep entrainment into the mantle (Scholl and von Huene, *in press*). These two processes exert some control over the package of materials that is subducted beyond forearc regions and are thus capable of influencing geochemical evolution at subarc and greater depths (Morris and Ryan, 2003; Li and Bebout, 2005; Scholl and von Huene, *in press*). The possibility that the mélange zones in some HP suites are a common product of the complex deformation and geochemical mixing along the slab–mantle interface (e.g., Bebout and Barton, 2002; Breeding et al., 2004; King et al., 2006; Spandler et al., *in press*) warrants further consideration (Fig. 1), and mélange zones consisting of hydrated mixtures of sediment, oceanic crust, and mantle rocks could contribute to low seismic velocity anomalies at/near the tops of subducting slabs (Peacock and Hyndman, 1999; Abers, 2005). There has been considerable recent discussion of the possibility that the ultramafic part of the subducting lithosphere is extensively hydrated and metasomatized as a result of plate-bending near trenches (Ranero et al., 2005), and that the slab–mantle interface could be infiltrated by large amounts of fluid emanating from these sub-crustal ultramafic rocks (Rupke et al., 2004; Tenthorey and Hermann, 2004; Ranero et al., 2005; Fig. 1).

## 3. Metamorphic record of subduction-zone chemical cycling

High-pressure and UHP suites owe their present existence at the surface to complex combinations of faulting and buoyancy-driven ascent (Jolivet et al.,

2003; Tsujimori et al., 2006; Ernst, 2006), and a number of UHP suites contain oceanic rocks that were first deeply subducted, then exhumed relatively rapidly during later continent–continent collisions (e.g., Western Alps; Ernst, 2006). Their mineral assemblages, textures, and geochemistry preserve histories of their seafloor origins, prograde recrystallization, and later exhumation, and if studied with care, these rocks can potentially provide detailed geochemical records of metasomatic processes operating at depth in subduction zones. In this section, I summarize some recently published examples of geochemical information that can be obtained through study of such rocks, stressing the need for careful merging of any geochemical work with the metamorphic petrology of the rocks.

In general, subduction-zone metasomatism can be imagined as occurring over a wide range of scales (sub-micron to kilometer) via varying combinations of mechanical mixing, diffusional, and fluid- and melt-mediated mass transfer processes. Schmidt and Poli (2003) provide a recent synthesis of information regarding prograde metamorphic reaction histories of subducting rocks, including those having larger effects on the redistribution of trace elements of interest in studies of crust–mantle cycling (also see Bebout, *in press*). A growing number of studies have focused on evaluation of HP and UHP devolatilization and fluid compositions, in part using observations from vein arrays (Becker et al., 1999; Widmer and Thompson, 2001; Scambelluri and Philippot, 2001; Brunsmann et al., 2001; Rubatto and Hermann, 2003; Molina et al., 2004; Spandler and Hermann, 2006), fluid inclusions (Touret and Frezzotti, 2003), and stable (and to a lesser extent, radiogenic) isotope systems (Nakano and Nakamura, 2001; Zheng et al., 2003; Zack et al., 2003; Bebout and Nakamura, 2003; John et al., 2004; Bebout, *in press*). Here, I focus mostly on the recently expanded major and trace element dataset for HP and UHP metamorphosed oceanic crust and seafloor sediment (see the summary of localities, and sources of data, in Table 2), emphasizing relationships among the concentrations of elements that have recently been used to trace contributions of subduction to arc lavas and deeper mantle heterogeneity (these elements include B, the large-ion lithophile elements [LILE], the light rare-earth elements [LREE] and middle rare-earth elements [MREE], U, Pb, and Th). In most cases, I present data as element ratios thought not to be fractionated by partial melting in the mantle (e.g., Ba/Th, K/Th, Ce/Pb, Th/U, Nb/U, Rb/Cs), that is, ratios for which values for mantle-derived lavas (arc lavas, ocean island basalts) reflect the values of their source regions rather than reflecting later

igneous fractionations in the ascending and crystallizing lavas. I also emphasize parent–daughter element ratios for which change during subduction-zone metamorphism could exert control on arc lava compositions and the long-term isotopic evolution of the deeper mantle (e.g., Sm/Nd, and ratios among U, Th, and Pb). Overall, the whole-rock geochemical variations presented here are a representation of the range of compositions that can be produced by the aggregate seafloor alteration and subduction-zone metamorphic processes, to depths of approximately those beneath volcanic fronts (~90 or so km; Fig. 3).

### 3.1. Records of metasomatism in HP/UHP metabasalts and metagabbros

Geochemical studies of HP and UHP of metabasaltic lithologies have concentrated on either variably metasomatized metabasaltic blocks in *mélange* (Sorensen et al., 1997; Bebout and Barton, 2002; Spandler et al., 2003, 2004; Saha et al., 2005; King et al., 2006; Spandler and Hermann, 2006; King et al., 2007; see sketch of blocks in *mélange* in Fig. 1) or larger, more coherent tracts of metabasalt not obviously related to *mélange* zones and in many cases showing very little evidence for deformation (Becker et al., 1999; Widmer and Thompson, 2001; Brunsmann et al., 2001; Zack et al., 2001; Rubatto and Hermann, 2003; Chalot-Prat et al., 2003; Zack et al., 2003; John et al., 2004; Molina et al., 2004). These previous studies have mostly focused on whole-rock compositions, but some have undertaken single mineral analyses by electron microprobe, LA-ICPMS (laser ablation inductively coupled plasma), and SIMS (secondary ion mass spectrometry), allowing the identification of key mineral phases (in some cases, accessory phases) hosting trace elements of interest, or have involved fluid inclusion or isotopic analyses (Brunsmann et al., 2001; Zack et al., 2001; John et al., 2004; Spandler et al., 2004). In general, studies of metabasaltic blocks in *mélange* (inferred to be zones of enhanced fluid flow; see Fig. 1) document extensive fluid–rock interaction resulting in element mobility in HP or UHP fluids and the development of metasomatic “rinds” on the rims of these blocks (Sorensen et al., 1997; Bebout and Barton, 2002; Breeding et al., 2004; Saha et al., 2005). The work on the larger, coherent tracts of metabasalt (perhaps a better representation of intact oceanic slabs) has for the most part concluded that, in forearcs, fluid and element mobility in the slab is limited in scale, leaving little or no record of its passage, and that any element release or addition has largely been obscured by uncertainty

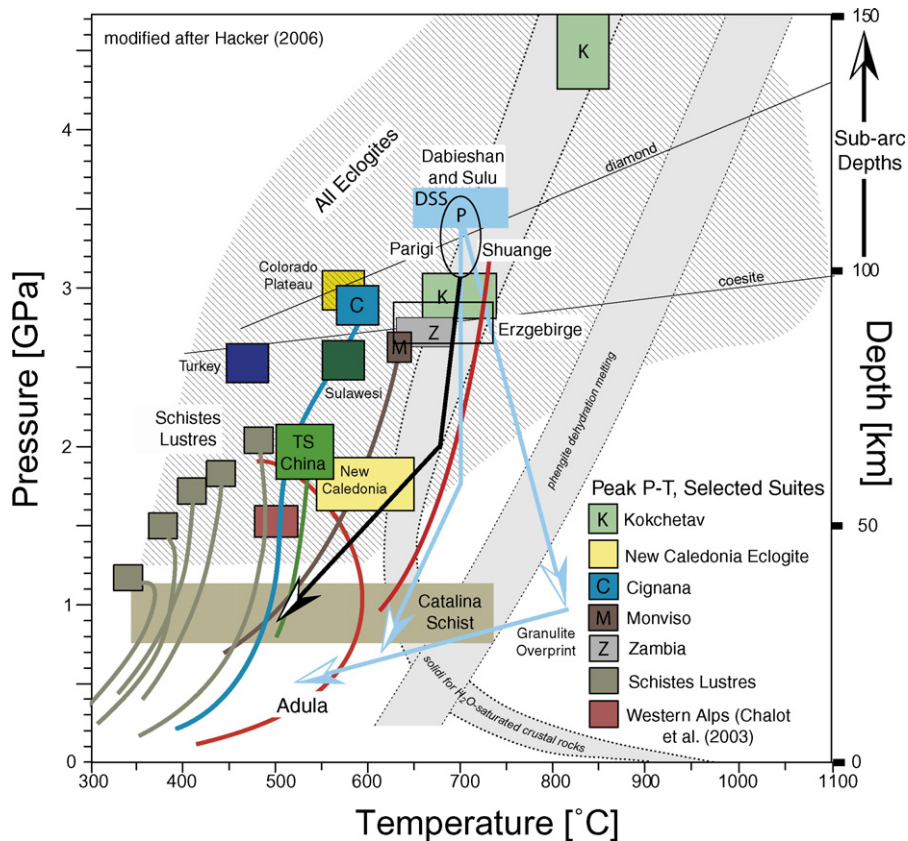


Fig. 3.  $P$ – $T$  diagram showing regions of peak metamorphism and exhumation paths (lines indicating  $P$ – $T$  history of rocks during their transit toward the surface) for selected HP and UHP metamorphic suites discussed in the text (see Table 2) and for which data are presented in Figs. 4, 5 and 7 (modified after Hacker, 2006; sources of peak  $P$ – $T$  data and paths therein and, for some suites, in Table 1). Note that many of these suites experienced down-temperature (“cool”) exhumation paths affording preservation of mineral assemblages related to their prograde subduction history — the rapid exhumation of these rocks is most spectacularly represented by the preservation of lawsonite (in lawsonite–eclogite), coesite, and microdiamond in some of the UHP suites. Examples of lawsonite–eclogite include rocks in Turkey, Sulawesi, and the USA Colorado Plateau (the latter as xenoliths in diatremes; see Tsujimori et al., 2006; Usui et al., 2006). The region labeled “TS” indicates the peak  $P$ – $T$  for rocks at Tianshan, China (see Tsujimori et al., 2006). The multiple exhumation paths taken by rocks in the Dabieshan–Su–Lu belt (in light blue, with arrows) are from Zheng et al. (2003), and Franz et al. (2001). Note that a number of suites experienced peak  $P$ – $T$  straddling the “wet” solidus for melting of mafic and sedimentary rocks (see gray-shaded zone labeled, “solidi for  $H_2O$ -saturated crustal rocks”) — these suites are candidates for study aimed at ascertaining the geochemical effects of partial melting (see Hermann et al., 2006).

regarding the composition of the protolith (Widmer and Thompson, 2001; Chalot-Prat et al., 2003; Spandler et al., 2003, 2004; John et al., 2004). Studies of veining and isotopic records of fluid–rock interactions have also generally concluded that fluid fluxes are low (recent discussion by Spandler et al., 2003; John et al., 2004; Hermann et al., 2006; Spandler and Hermann, 2006) resulting in the preservation of seafloor alteration patterns (Cartwright and Barnicoat, 1999). This previous work points to the possibility that fluid flux representing the aggregate of small amounts of fluid loss in such sections at a local scale could be focused in its transport (at far higher fluid fluxes) along zones of structural weakness, thus concentrating metasomatism along these

zones (cf. Bebout and Barton, 2002; Spandler et al., 2003, 2004; Breeding et al., 2004; John et al., 2004; King et al., 2006, 2007; Spandler et al., in press).

The plots in Fig. 4 provide some examples of the general tendency for geochemical compositions of metabasaltic rocks subducted to depths of up to  $\sim 100$  km to overlap strongly with the compositions of their protoliths, the variably hydrothermally altered basalts on the seafloor, indicating minimal change in the compositions of these rocks as a result of forearc metamorphism and related fluid–rock interactions. In these plots, the data from Sorensen et al. (1997), Saha et al. (2005), and Spandler et al. (2004) are for samples of mafic tectonic blocks in mélangé zones, some with

Table 1  
Glossary of terms used in this paper

Altered oceanic crust	(AOC) Upper part of the seafloor oceanic crust chemically altered by interactions with seawater
Arc magma	Silicate melt formed by melting in the mantle wedge hanging wall above subducting slabs, arc lavas if they erupt at the surface
Arc source regions	Region in mantle wedge hanging wall of a subduction zone in which partial melting occurs to form arc magmas (Fig. 1)
Arc volcanic front	The position of the arc volcanoes nearest the trench
Exhumation	Processes by which rocks formed at depth are brought to the surface
Fluid	Disordered, non-crystalline phase consisting of particles in motion and possessing unspecified composition, commonly rich in molecules such as H <sub>2</sub> O and CO <sub>2</sub> and containing dissolved major and trace elements
HP and UHP metamorphism	High-pressure and Ultrahigh-pressure metamorphism, corresponding to rocks metamorphosed at approximate pressures of 0.5–1.5 GPa and >1.5 GPa, respectively (see Carswell and Compagnoni, 2003)
Mechanical mixing	Simple, physical mixing of materials, at the grain scale, in response to strong deformation
Mélange zone	Strongly deforming zone in which various rock types are physically mixed and chemically altered and commonly containing more intact remnants of the rocks being incorporated (as tectonic blocks)
Metamorphic petrology	The study of solid-state mineralogical, textural, and geochemical changes in rocks as they experience changing conditions, generally largely in response to changes in pressure and temperature
Metasomatic rinds	Concentric shells of chemically altered rock formed at the margins of tectonic blocks in mélange zones
Metasomatism	Processes changing the bulk chemical composition of a rock, in many cases involving interaction with fluid
Mid-ocean ridge basalt	(MORB) Basalt that forms the upper part of the oceanic crust formed at mid-ocean ridges
Ocean island basalt	Basalts restricted to islands that are not related to subduction, and that are in many cases related to hot spots
Oceanic lithosphere	Tectonic plate typically about 50–100 km thick, consisting mainly of mafic crust (6–7 km thick) and ultramafic mantle
Ophiolite	On-land exposure of ancient oceanic crust, in some cases having been metamorphosed before emplacement
Parent–daughter element ratio	Ratio of trace elements in which one of the elements decays to form isotopes of the other element
Partitioning	Distribution of a trace element between different phases
Primitive mantle	Silicate portion of the Earth as it existed after separation of the core but before it differentiated into crust and present-day mantle
Protolith	The pre-metamorphic lithologic precursor to a metamorphic rock
Radiogenic isotope system	Isotope system in which a nuclide or multiple nuclides are formed by radioactive decay of another nuclide(s)
Subducting slab	Generally an oceanic tectonic plate that sinks below an over-riding continental or oceanic plate
Supercritical liquid	A fluid stable at <i>P</i> and <i>T</i> greater than the critical point or curve in the system (see Manning, 2004)
Volatiles	Compounds that form low-viscosity fluids when released from a rock or magma

metasomatic rinds developed at their margins. These rinds, believed to have developed during fluid–rock interactions in the mélange at HP or UHP metamorphic conditions, provide the clearest fingerprint of the geochemical alteration attributable to subduction zone metamorphism. The data from Marschall (2005), King et al. (2004), and John et al. (2004) are for samples collected from larger expanses of coherent metabasalt away from any mélange zones and perhaps more representative of the coherent oceanic slab as it subducts. In each of the plots in Fig. 4, data for the metabasaltic rocks from these two settings are compared with data for fresh (unaltered) MORB and for various seafloor altered basalts (AOC; sources of data in figure caption), with the arrows on each plot distinguishing the chemical trends associated with HP and UHP metamorphism from the alteration associated with seafloor alteration.

Potassium and Rb show large co-enrichments both on the seafloor and during subduction-zone metamorphism, as demonstrated by the nearly complete overlap of K–Rb

trends in data for altered oceanic crust (AOC; DSDP/ODP Sites 417/418, 504B, 801C, and 1149) and for both the metabasaltic rocks from more coherent exposures and the metasomatic rinds on tectonic blocks (Fig. 4A). Few of these metabasaltic samples have K–Rb concentrations lower than those of unaltered MORB and the AOC; however, significant HP and UHP metamorphic K–Rb losses could be obscured by uncertainty in the extent of seafloor alteration. In contrast with this rather frustrating relationship, Ba exhibits differing enrichment patterns, relative to those of K (and Rb), for seafloor and subduction-zone metasomatic alteration, seemingly providing one means of distinguishing between the two metasomatic histories (see the two trends in Fig. 4B; cf. Sorensen et al., 1997, 2005). As Becker et al. (2000) noted, some metabasalts do have K/Th and Ba/Th lower than these ratios in various AOC and fresh basalt estimates, conceivably related to decrease in K and Ba, relative to Th, during metamorphic dehydration (see Fig. 4B). Spandler et al. (2004) provided a more thorough consideration of the protoliths of high-P

metamafic rocks from New Caledonia (see data in Fig. 4B), and concluded that there is little evidence for LILE loss from these rocks during subduction zone metamorphism when each unit from this locality is compared in composition with its likely protolith (inferred protoliths include enriched and normal mid-ocean ridge basalt, back-arc basin basalt, alkaline basalt, plagioclase-rich cumulate, seafloor-altered basalt and Fe–Ti basalt).

Fig. 4C–E demonstrate some relationships for Ce–Nb–U–Th–Pb concentrations similar to those for the LILE, and some possible evidence for mobility of Pb and Th in HP and UHP fluids or melts. John et al. (2004) suggested that the deviations in their Ce–Pb data (Fig. 4C) from compositions of oceanic basalts (MORB and OIB) represent Pb additions during two stages of subduction-related alteration, one at peak metamorphic conditions and one during exhumation (see the arrows representing alteration trends for “John GI ECL” and “John GIID ECL” on Fig. 4C). However, Fig. 4C demonstrates similar trends for the extremely low-grade metabasalts in the External Units in the Alps (“Chalot Alps EXT”; metamorphosed at very low grade but not subducted; Chalot-Prat, 2005) and for some AOC (e.g., some of the data for Site 1149). Seafloor alteration of basalt has long been known to produce enrichments in U, relative to REE, HFSE, Pb, and Th (Nb–U data for AOC in Fig. 4D; Staudigel, 2003). Deviations in the Nb/U of HP and UHP metabasalts from that of MORB due to subduction-zone metamorphism are difficult to demonstrate, as nearly all of the data for the metabasalts lie within the fields for AOC, and like the plots of the LILE, very few metabasaltic samples show obvious evidence for subduction-zone depletion in U relative to fresh MORB (i.e., few data fall to the upper left part of the plot in Fig. 4D). A small number of metabasaltic rocks, particularly the Group IID eclogites of John et al. (2004), show hints of U loss relative to Th, leading to higher Th/U relative to both MORB and AOC—these rocks are believed to have been metasomatized along zones of enhanced fluid infiltration during HP metamorphism (see Fig. 4E). In Fig. 4E, Th–U data for metasomatic rinds on mafic tectonic blocks (particularly “Sorensen” and “Saha”), again, the clearest fingerprint of subduction-zone chemical alteration, seemingly reflect Th additions by HP and UHP metamorphic fluids, as they fall to the right of the seafloor alteration trend (see the gray arrow indicating the trajectory of metamorphic enrichment). Finally, the data in Fig. 4F demonstrate some possible loss of LREE (here represented by Nd) during HP metamorphism, relative to MREE (here

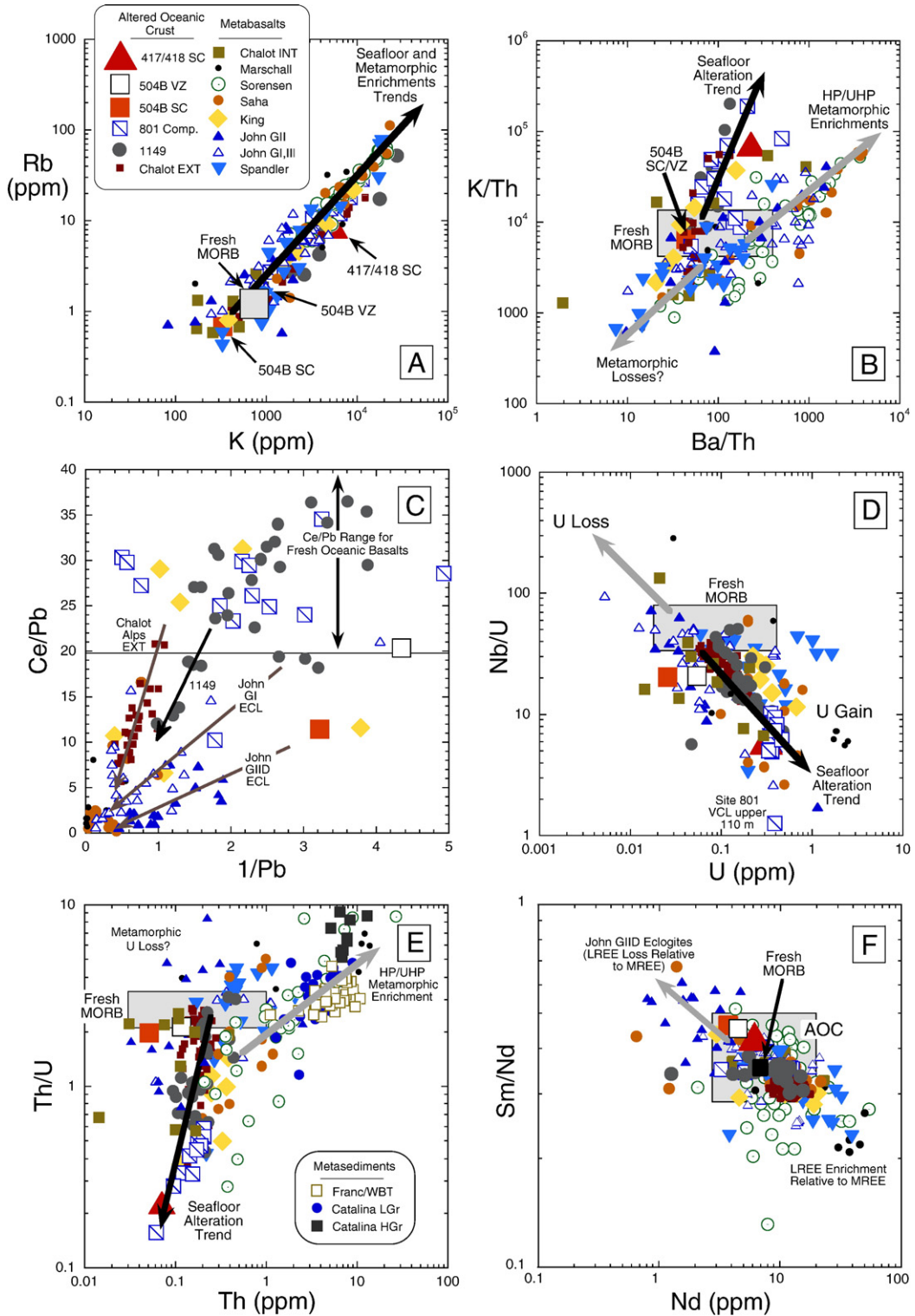
represented by Sm), as indicated by a shift to higher Sm/Nd at lower Nd concentrations for the Group IID eclogites of John et al. (2004) thought to have experienced enhanced fluid–rock interactions. However, the Sm–Nd data for most HP and UHP metabasalts either overlap the range of data for N-MORB and various AOC or show some shift to higher Nd concentrations and lower Sm/Nd consistent with some LREE enrichment during metamorphism.

### 3.2. Effects of devolatilization on the compositions of deeply subducted sediments

Recently conducted work on trace element compositions and devolatilization in several subduction-related metamorphosed sedimentary suites appears to shed some light on the issue of the efficiency of deep subduction of trace elements in subducted sediments. The Catalina Schist contains metasedimentary units that were subducted along prograde  $P$ – $T$  paths ranging from very cool paths, similar to those predicted by thermal models of modern subduction, to paths that are anomalously warm for most modern subduction zones, for the amphibolite facies unit, sufficiently warm to result in partial melting (see Fig. 5A; see Bebout et al., 1999, 2007). Whereas some trace elements thought to be relatively mobile in fluids (Cs, B, As, Sb, and N) show dramatic depletion in the rocks that experienced the higher-temperature paths (epidote–blueschist, epidote–amphibolite and amphibolite), the rocks experiencing the cooler paths largely retain these elements (lawsonite–albite and lawsonite–blueschist rocks). This observation is consistent with the retention of these elements to depths of up to  $\sim 45$  km in most modern subduction zones (also see Sadofsky and Bebout, 2003). Fig. 5B and C demonstrate relationships among Rb, Cs, B, and Li concentrations in white micas (phengite), the dominant mineral reservoir for these elements, and compare these data with the whole-rock data for Rb and Cs concentrations in the Schistes Lustres and Lago di Cignana metasedimentary rocks (see the shaded horizontal field in Fig. 5C). Busigny et al. (2003) suggested that N, H, and Cs were retained in metasedimentary rocks in the Schistes Lustres and at Lago di Cignana subducted along relatively cool  $P$ – $T$  paths to depths of  $\sim 60$ – $90$  km (see peak  $P$ – $T$  conditions and exhumation paths for the Schistes Lustres in Fig. 3), approaching the depths beneath volcanic fronts (Busigny et al., 2003; cf. Bebout et al., 2004; see Fig. 5C). Together, the observations from the Catalina Schist and Alpine suites indicate that, in cool margins, these elements are largely available for addition to the mantle wedge beneath arcs.

Depletion of elements such as Ba, Th, La, and Sm (used as tracers of sediment inputs in arc lavas, and in studies of deeper mantle geochemical heterogeneity; Plank,

2005) is not evident in these suites (and other HP metapelitic rocks; see Arculus et al., 1999; Spandler et al., 2003), and melting at greater depths is perhaps





required for more significant removal and fractionation of these elements.

### 3.3. Geochemical hybridization in *mélange* zones

Geochemical work on *mélange* zones, including the metasomatic rinds on tectonic blocks, indicates that these are zones of high fluid flux, channelways which focus fluid flow and produce isotopic homogenization and disproportionately metasomatized lithologies (Sorensen et al., 1997; Bebout and Barton, 2002; Breeding et al., 2004; Saha et al., 2005; King et al., 2006, 2007; Spandler et al., in press; see Fig. 1). The existing geochemical data for *mélange* demonstrate that complex mechanical and metasomatic mixing processes in these zones are capable of producing rocks rich in volatiles and with unusual, hybridized major and trace element and isotopic compositions (e.g., extremely chlorite-, talc-, and amphibole-rich rocks; see Bebout and Barton, 2002; Breeding et al., 2004; King et al., 2006, 2007; Spandler et al., in press). Fluid–rock interactions in such zones could result in the release of fluids with chemical and isotopic compositions reflecting these hybridized compositions. These fluids could simultaneously geochemically resemble sediment-derived fluids and AOC-

derived fluids, confounding studies of volcanic arc geochemistry in which researchers attempt to determine sources of fluid and their relative proportions.

### 3.4. Summary comments regarding element mobility during HP/UHP metamorphism

The growing geochemical database for HP and UHP metabasaltic and metasedimentary rocks (including data for veins, metasomatic rinds, fluid inclusions, and *mélange* zones) demonstrates at least local-scale mobility of LILE (K, Rb, Cs, Ba, Sr), U, Th, Pb, B, and perhaps also Li and LREE in crust and sediment subducted to depths of  $\sim 90$  km approaching the depths beneath volcanic fronts. However, this element mobility evidently represents relatively small fractions of loss distributed over large volumes of rock, perhaps leading to a significant flux, but in many cases without an obvious depletion signature left in their sources. The generalization regarding the lack of obvious element loss in metabasaltic rocks, and depletions of only the most fluid-mobile elements in sedimentary rocks, is consistent with experimentally-derived fluid-mineral partitioning data that seemingly indicate that relatively large fluid fluxes are necessary to produce observable

Fig. 4. Whole-rock element concentrations in metabasaltic rocks from HP and UHP metamorphic suites. These plots allow comparisons of the compositions of HP and UHP metabasalts (see summary of the suites plotted here in Table 2) with compositions of “fresh” (unaltered) seafloor basalts and AOC. (A, B) Relationships among concentrations of K, Rb, Ba, and Th for HP and UHP metabasalts and their presumed seafloor protoliths. In these figures, data for AOC from DSDP/ODP Sites 417/418 (composite composition from Staudigel, 2003), 504B (supercomposite and volcanic zone composite from Bach et al., 2003), and 801C (various sub-composites) and 1149 (data for individual samples; data for both from Kelley et al., 2005), are used to define chemical trajectories associated with seafloor hydrothermal alteration that can be considered when evaluating any changes in chemical compositions due to subduction-zone metamorphism (see arrows labeled, “Seafloor Alteration Trend”; shown as a field in F). Data for metasomatized tectonic blocks in *mélange*, and the metasomatic rinds developed on these blocks, from John et al. (2004), Saha et al. (2005), Sorensen et al. (1997), and Spandler et al. (2004) best define alteration trajectories that can be related directly to HP and UHP metamorphism. Data from King et al. (2004), John et al. (2004), and Marschall (2005) are for samples from more intact exposures of HP or UHP metamorphosed AOC. Most of the samples for which data are presented here have major and fluid-immobile trace element compositions similar to those in MORB, that is, deemed representative of magmatic products at mid-ocean ridges (including their Nd isotope compositions indicating their production in the depleted mantle; see Table 1). Several authors have, in more detail, related the compositions to expected spreading center differentiation trends (John et al., 2004; Spandler et al., 2004). Only the studies by Becker et al. (2002) and Arculus et al. (1999) invoke significant whole-rock loss of LILE during metamorphism of AOC (see text for discussion). The composition of “Fresh MORB” (N-MORB) in (A) is from Sun and McDonough (1989). The elevated Ba enrichments in many HP and UHP metamorphic lithologies could reflect transfer of sedimentary Ba into subducting oceanic crustal lithologies in which high Ba/Th, Ba/La, and Ba/Nb signatures could then be entrained to greater depths. (C) Ce–Pb relationships for HP and UHP metabasalts and their presumed seafloor protoliths (after Miller et al., 1994; John et al., 2004). Arrows toward the origin indicate possible trends of Pb addition (and resulting decrease in Ce/Pb) during seafloor alteration (“1149”), very low-grade metamorphism related to ophiolite emplacement (“Chalot Alps EXT”), or possibly HP and UHP metamorphism (“John GI ECL” and “John GIID”; discussion by John et al., 2004). Data for HP metamorphic rocks from Marschall (2005) and Saha et al. (2005) seemingly also indicate Pb additions, perhaps during HP/UHP metamorphism. (D) Nb–U data for HP and UHP metabasalts in comparison with data for AOC and unaltered “fresh” MORB, demonstrating the overlap of the metabasaltic compositions with compositions attributable to seafloor alteration. (E) Th–U relationships for HP and UHP metabasaltic rocks in comparison with fresh MORB, AOC, and metasedimentary rocks from the Catalina Schist and from the Franciscan Complex and Western Baja Terrane. Note that the high-grade (amphibolite-facies) metasedimentary rocks in the Catalina Schist (black filled squares labeled, “HGrCSSed”) have elevated Th/U, relative to their low-grade equivalents, possibly reflecting removal of low-Th/U “fluids” (hydrous fluids or silicate melts). The gray arrow indicates a possible trend of Th enrichment, resulting in increased Th/U in some metabasaltic samples (e.g., data from Sorensen et al., 1997; Saha et al., 2005). (F) Sm–Nd data for HP and UHP metabasalts, rinds, and AOC, as an example of a parent/daughter element pair possibly disrupted by subduction-zone metamorphism. It is evident that Sm/Nd can be shifted to higher or lower values, and the shifts to higher values are consistent with recent experimental work indicating that Nd is more strongly partitioned into hydrous fluids than Sm (see Kessel et al., 2005a).

Table 2

Summary of HP and UHP metamorphic suites for which data are presented in this paper

Suite/location		Peak $P$ – $T$ (see Fig. 3)	Lithology (protolith)	Geochemical work done <sup>c</sup>	Reference
Alps Internal Massif <sup>a</sup>	Italy/France	1.5 GPa 475–525 °C	MORB	M,T,SrNdIsot $\epsilon_{\text{Nd}}(t)=7$ –10	Spandler et al. (2003)
Syros	Greece	0.6–0.7 GPa 400–430 °C	MORB	M,T $\epsilon_{\text{Nd}}(t)=7$ –9	Marschall (2005) Brockner and Enders (2001)
Dominican Republic Franciscan Complex (and Oregon, Baja)	Various	0.8–1.1 GPa 500–700 °C	MORB (+Rinds)	M,T For Franciscan, $\epsilon_{\text{Nd}}(t)=8$ –10	Sorensen et al. (1997) Nelson (1995)
Franciscan Complex	California	Various <sup>b</sup> (see Saha et al., 2005)	MORB, OIB? (+Rinds)	M,T,PbIsot $\epsilon_{\text{Nd}}(t)=8$ –10	Saha et al. (2005) Nelson (1995)
Lago di Cignana	NW Italy	2.9 GPa, 625 °C	MORB	M,T,SIMS $\epsilon_{\text{Hf}}(t)=13$ –14 $\epsilon_{\text{Nd}}(t)=9$	King et al. (2004) Cluzel et al. (2001) Amato et al. (1999)
Zambia	Africa	2.6–2.8 GPa 630–690 °C	MORB	M,T $\epsilon_{\text{Nd}}(t)=6$ –8, $\epsilon_{\text{Hf}}(t)=10$ –15	John et al. (2004)
New Caledonia		1.9 GPa ~600 °C	MORB and other	M,T, LAICPMS $\epsilon_{\text{Nd}}(t)=3$ –11	Spandler et al. (2004) Cluzel et al. (2001)
Catalina Schist	California	Multiple units (see Figs. 3,5)	Sedimentary	M,T,SIMS,Nisot metabasalt $\epsilon_{\text{Nd}}(t)=9$ –11	(Bebout et al., 1999, 2007)
Schistes Lustres	NW Italy (Cottian Alps)	Multiple units (see Fig. 3)	Sedimentary	M,T,SIMS,Nisot	(Busigny et al., 2003; Bebout et al., 2004)

<sup>a</sup> Very low grade MORB-derived equivalents (External Units of W. Alps), with  $\epsilon_{\text{Nd}}(t)=8$ , investigated by Chalot-Prat (2005).

<sup>b</sup> Higher-grade metabasaltic blocks floating in low-grade melange matrix (peak pressures mostly <1.5 GPa).

<sup>c</sup> M=major elements; T=trace elements; Isot=isotope data.

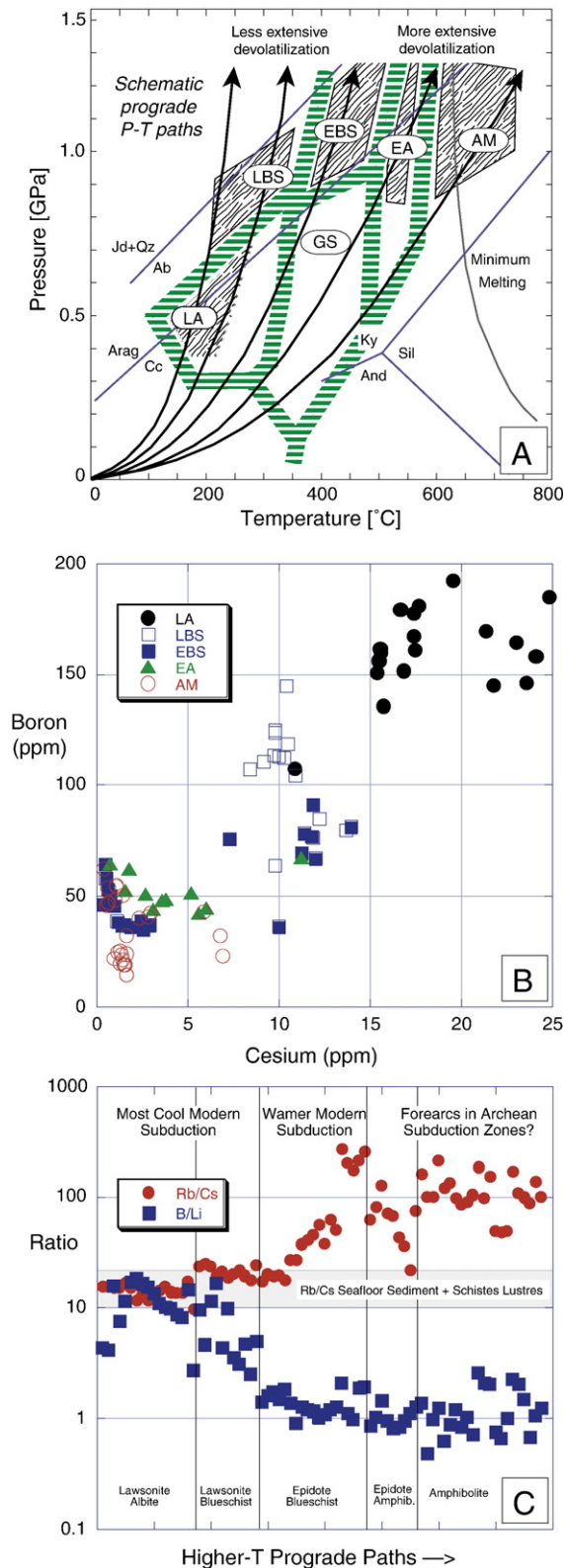
element depletions at the pressures and temperatures at which these fluids would predominantly be the more dilute aqueous fluids (Zack et al., 2001; Hermann et al., 2006). Only the zones of enhanced fluid flux would be expected to bear obvious signatures of element gains and losses (John et al., 2004), and disproportionate element release could occur in the more permeable mélange zones facilitating larger fluid flux (Bebout and Barton, 2002; King et al., 2006; Spandler et al., in press). Supercritical liquids and hydrous silicate melts, likely produced at the higher  $P$  and  $T$  beneath volcanic fronts and across arcs, appear capable of mobilizing larger fractions of the element inventory in all of these rocks types (Kessel et al., 2005a; Hermann et al., 2006).

#### 4. Compatibilities with arc geochemistry

From an arc geochemist's perspective, the forearc could be viewed as a metamorphic "filter" either preventing or allowing the retention of relative fluid-mobile components to depths beneath the volcanic front, where they could then contribute to volcanic front and cross-arc geochemistry (Morris and Ryan, 2003; Bebout, in press). Studies of metasedimentary rocks appear

to demonstrate remarkable retention even of elements such as B and Cs, thought to partition strongly into aqueous fluids, to depths of up to 90 km in relatively cool subduction zones (Sadofsky and Bebout, 2003; Busigny et al., 2003; Bebout et al., 2007). The majority of the existing data for progressively metamorphosed HP/UHP metabasaltic and metagabbroic rocks similarly point to efficient retention of many of the elements of interest as "slab tracers" to depths beneath the volcanic front (~100 km or more; (Schmidt and Poli, 2003; Bebout, in press). The correlations between inferred subduction fluxes of less-fluid-mobile trace elements (particularly K, Ba, Rb, Sr, and Th) in subducting sediments and corresponding arc lavas (in particular, Ba and Th) are certainly also compatible with the retention of the bulk of these element inventories to depths beneath arcs (Plank et al., 2002; Plank, 2005) and some commonality, from arc to arc, in the mechanisms by which this element inventory is delivered into arcs.

For some particularly fluid-mobile elements, such as Cs, B, As, and Sb, concentrations in arc lavas produced in "cooler" subduction zones are higher than those in arc lavas from "warmer" subduction zones (expressed as having higher ratios of these elements to less fluid-mobile elements with similar incompatibility during



partial melting in the mantle wedge; e.g., B/Be, Cs/Th, As/Ce, Sb/Ce; see Bebout et al., 1999; Morris and Ryan, 2003; Bebout, in press). The warmer margins, for example Cascadia and SW Japan (see Bebout et al., 1999; Peacock and Wang, 1999; Stern, 2002), show lower arc enrichments in these so-called “fluid-mobile elements” presumed to reflect the removal of these elements in the relatively warm forearc (see Bebout et al., 1999). Accordingly, the data in Fig. 5 seemingly indicate that, in subduction zones where sediment prograde  $P$ - $T$  paths pass through the epidote–blueschist facies (or higher- $T$  facies), considerable loss of B and Cs will occur during subduction to  $\sim 45$  km depths, thus preventing the delivery of these elements to the depths beneath volcanic fronts. Although the variations with increasingly higher- $T$  prograde paths observed in suites such as the Catalina Schist (and other HP/UHP suites; see Moran et al., 1992; Busigny et al., 2003) serve as an analogue to what might occur at similar temperatures but at higher pressures, it must be remembered that these suites do not directly represent processes beneath arcs. The cross-arc variations in some isotope and trace element ratios (see review by Morris and Ryan, 2003) are tantalizing evidence, however, that metamorphism results in “distillation” of some components, perhaps resembling the losses in warmer units of the Catalina Schist, as subducting rocks traverse the subarc region (Fig. 1; see Bebout et al., 1999; Bebout and Nakamura, 2003; Bebout et al., 2007). These cross-arc variations have been interpreted as reflecting diminishing fluid additions, changing compositions of the fluid additions related to progressive element loss, and/or changes in the proportions of aqueous fluids and silicate melts across individual arcs toward the back-arc (see discussions by Bebout et al., 1999; Morris and Ryan, 2003; Bebout and Nakamura, 2003; Bebout et al., 2007). The recently proposed transitions with depth in the physical

Fig. 5. Demonstration of varying change in LILE, B, and Li for metasedimentary rocks as a function of the prograde  $P$ - $T$  path along which the rocks were metamorphosed. (A) Simplified  $P$ - $T$  diagram demonstrating the range of prograde paths experienced by the units in the Catalina Schist. Rocks experiencing the high-temperature paths show more extensive loss of volatiles than the rocks experiencing the low-temperature paths (Bebout et al., 1999, 2007; Bebout, in press). (B) B and Cs concentrations in white micas in the metasedimentary rocks of the Catalina Schist, showing decrease in both in the rocks which experienced the higher- $T$  prograde paths (see A). (C) Change in B/Li and Rb/Cs resulting from the loss of B and Cs, at higher grades, relative to Li and Rb, both of which show little change with increasing grade. Also shown (in gray-shaded horizontal field) is the range of Rb/Cs for seafloor sediment (data from Ben Othman et al., 1989; Plank and Langmuir, 1998) and the Schistes Lustres (data from Busigny et al., 2003).

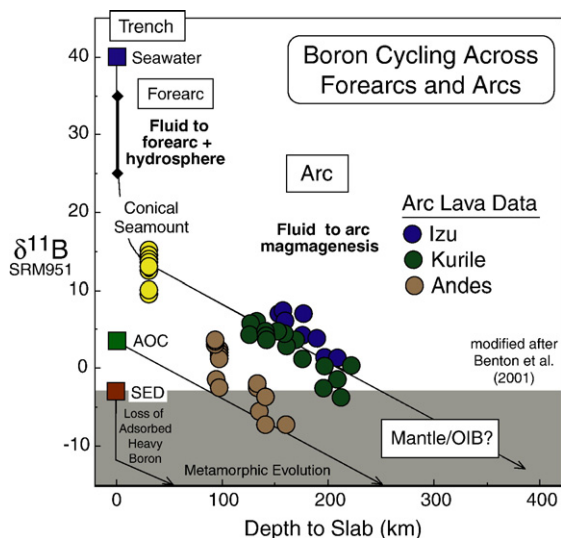


Fig. 6. Cross-arc B isotope evolution, modified after Benton et al. (2001), taking into account compositions of near-trench fluids, seawater, altered oceanic crust and seafloor sediment (before and after loss of high- $\delta^{11}\text{B}$  adsorbed B), data for cross-arcs (Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Rosner et al., 2003), and approximate trends in  $\delta^{11}\text{B}$  (arrows) with prograde metamorphism of AOC and sediment (from the tourmaline-based model of Bebout and Nakamura, 2003). Loss of relatively isotopically “heavy” B from metamorphosing sediment and altered oceanic crust, in varying proportions, could produce the across-arc trends and result in the delivery of low- $\delta^{11}\text{B}$  residues into the deeper mantle.

and chemical transport properties of fluids from subducting materials (Kessel et al., 2005a; Hermann et al., 2006) will need to be considered in future geochemical studies of UHP suites potentially representing the residues of fluid and element removal at >100 km depths.

The model of trench-to-subarc (and beyond) cycling of B, and associated B isotope shifts set forth by Benton et al. (2001; Fig. 6) is a great demonstration of the exciting potential of multidisciplinary study aimed at “top to bottom” (seafloor to deep mantle) subduction cycling. This working model provides some direct and testable hypotheses regarding the evolution of B content and isotopic compositions in seafloor rocks subducted to beneath arcs, beginning with very early loss of isotopically heavy adsorbed B in sediments. According to this model, isotopically heavy B is lost from subducting rocks (presumably both altered oceanic crust and sediment; see Bebout and Nakamura, 2003), and this loss is likely to be primarily from micas (Bebout et al., 1999, 2007). Recently published fractionation factors for B isotopes between mica and fluid (Wunder et al., 2005) confirm the previous expectation regarding the direction and magnitude of this fractionation. At

greater depths beneath arcs, B cycling and isotopic evolution should continue to be strongly dictated by reactions involving mica, whether they involve aqueous fluids, silicate melts, or supercritical liquids. This further processing beyond the forearc could result in further decrease in arc lava  $\delta^{11}\text{B}$ , as proposed in studies of across-arc suites; (Morris and Ryan, 2003; see trends in Fig. 6).

The Li cycle in convergent margins, starting on the seafloor with early diagenetic processes and seafloor hydrothermal alteration, has also recently received considerable attention. Benton et al. (2004); (also see Moriguti and Nakamura, 1998; Tomascak et al., 2002; Elliott et al., 2004) suggested that, whereas B/Be and B isotopes in arc lavas record the latest fluid additions to the subarc mantle, Li isotope compositions of arc lavas appear to be buffered by the Li reservoir in the mantle, obscuring any subduction input signal for Li isotopes (see Wunder et al., 2006). As related to metamorphism, Zack et al. (2003) presented data for eclogites at Trescolmen (Adula Nappe) pointing to shifts in these deeply subducted mafic rocks to lower  $\delta^7\text{Li}$ , related to metamorphic devolatilization, that warrant further investigation particularly in light of the recently documented rapid diffusion of Li in clinopyroxene that could result in diffusive modification of any Li signal related to prograde metamorphism (Coogan et al., 2005).

## 5. On the horizon

Future study of the subduction-zone chemical pathway must concern itself with the degree to which the observations we make are lithologically biased—the rocks are, after all, rocks that did *not* get subducted into the deep mantle, that were fortuitously (and rapidly, to preserve even coesite and microdiamond; Fig. 3) brought to the surface, and so they are at best analogs of rocks that do enter the mantle. Another question concerns the scale of observations that become significant when considering the processes leading to arc magmatism. It is uncertain whether metasomatism of the types documented in our field studies liberates a sufficiently large element inventory in various “fluids” to satisfy mass-balance with arcs and produce volumetrically significant bulk change in the compositions of the more deeply subducting lithologies delivered in-bulk into the deeper mantle. Could volumetrically small, but highly metasomatized, fractions of the subducting package (e.g., mélangé or highly veined AOC or sediment) control the development of the deep-mantle signatures indicating subduction additions?

### 5.1. Microanalytical extraction of prograde geochemical records

The plots of whole-rock data presented in Figs. 4 and 5 are intended to illustrate some gross chemical trends, and obviously, more information comes from focused work in which sampling and analytical work is done fully in the context of textures and petrology. This work is increasingly being undertaken at finer scales, using microanalytical methods, and thus allowing discrimination between prograde and exhumation-related mineral assemblages and exploiting chemical and isotopic zoning in individual minerals (e.g., Zack et al., 2001, 2002; John et al., 2004; Spandler et al., 2004; Bebout et al., 2004; King et al., 2004; Bebout et al., 2007). Given that whole-rock element loss from such rocks is difficult to demonstrate due to protolith uncertainty, study of individual rocks at smaller scales could yield insight regarding chemical and isotopic evolution of the dehydrating lithologies, keeping in mind that even small amounts of loss, from large volumes of rock, could contribute significantly to forearc and arc element transfer. Such work can allow reconstruction of mineral reaction histories and related element redistribution (involving detailed geothermobarometry and calculation of segments of rock  $P$ – $T$  evolution), and can better resolve issues of vein formation and extents of open-system behavior in and near vein arrays (see Becker et al., 1999; Widmer and Thompson, 2001; Molina et al., 2004; Spandler and Hermann, 2006). Exhumation-related overprinting, and in some cases related chemical change, can place severe and frustrating restrictions on which suites are capable of providing details regarding geochemical evolution in deeply subducting rocks. In the worst cases, attempts to reconstruct prograde geochemical evolution are restricted to microanalytical work on a small number of mineral phases thought to be relatively chemically “robust” during exhumation, thus preserving prograde history (e.g., garnet, tourmaline, zircon, apatite, dolomite in the extensively retrograded metasedimentary rocks at the Lago di Cignana UHP locality (Reinecke, 1998; Bebout and Nakamura, 2003; Bebout et al., 2004; King et al., 2004).

Fig. 7 demonstrates a hand-specimen-scale microanalytical approach exploiting mineral chemical zoning in porphyroblasts, mineral assemblages within porphyroblasts and in rock matrices, exhumation-related overprinting deduced from textures, and veining relations (data for UHP metabasalts at Lago di Cignana are from King et al., 2004). Further work of this type ideally would be concentrated on high- $P/T$  rocks shown to

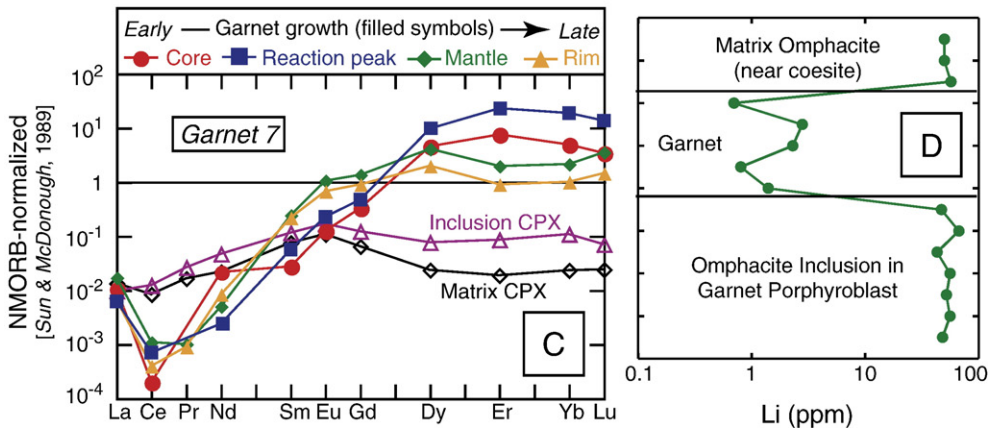
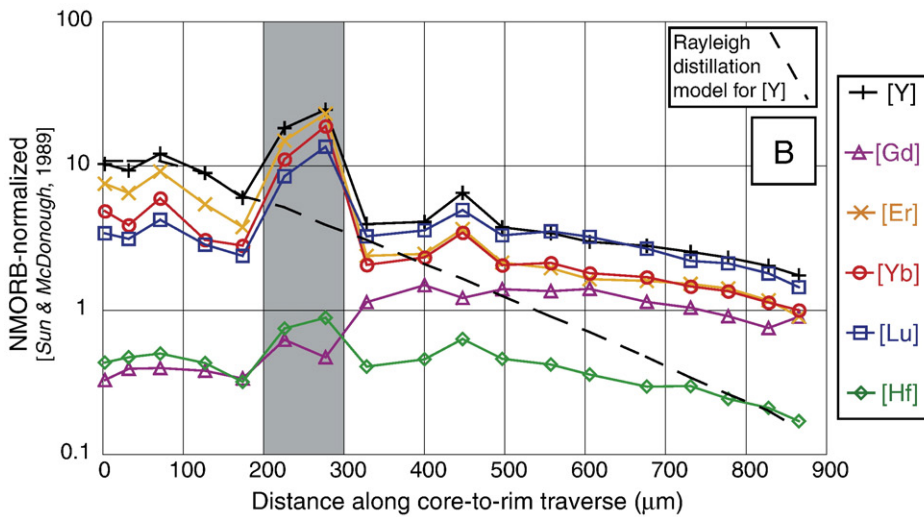
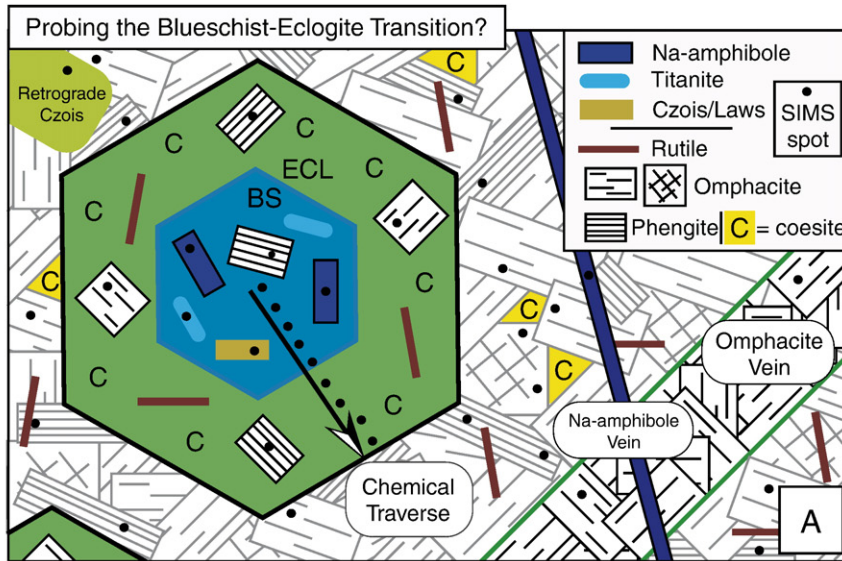
preserve prograde subduction history, with lower degrees of exhumation-related overprinting; however, this method allows one to focus work on phases reflecting the rock’s prograde history. For metabasaltic rocks, particularly promising suites have been identified, some which preserve even prograde lawsonite, in the central Erzgebirge, Germany (Massone, 2001), Turkey (Altherr et al., 2004), the Dominican Republic (Zack et al., 2004), and Su-Lu terrane (Kurahashi et al., 2001). The preservation of lawsonite in some of these rocks is indicative of particularly cool and rapid exhumation (Tsujimori et al., 2006), perhaps via buoyant ascent in forearc serpentinite diapirs. Analyses of chemical zoning patterns in porphyroblasts such as garnet and tourmaline can afford assessments of whole-rock trace element redistribution, in response to specific prograde reactions, and even stable isotope fractionation that occurred during fluid loss and evolution in mineral assemblages (e.g.,  $\delta^{11}\text{B}$  of tourmaline; perhaps also  $\delta^7\text{Li}$  across Li concentration profiles observed in some UHP metabasaltic and metasedimentary garnets (Nakano and Nakamura, 2001; Bebout and Nakamura, 2003; Bebout et al., 2004; King et al., 2004). However, the recently observed rapid Li diffusion in pyroxene (Coogan et al., 2005) should serve as a warning that we must, as a part of this microanalytical work, evaluate the extents of diffusion of the elements of interest (e.g., Li, B, N) in metamorphic minerals.

### 5.2. The physicochemical characteristics of slab fluids

Discussion of the physicochemical aspects of the slab fluids (see Manning, 2004; Hermann et al., 2006) ties in with the recent development of thermal models of subduction indicating that the slab–mantle interface may be at or near the “wet” solidus for partial melting of both sediments and the uppermost AOC (see Peacock et al., 2005). The partial compilation of geothermobarometry for eclogite suites in Fig. 3 demonstrates that the peak  $P$ – $T$  conditions calculated for a number of UHP suites fall near or above the wet solidi for partial melting of sediment and basalt, and geochemical work on UHP rocks can potentially yield insight regarding the nature of “fluids” produced at these conditions (see Hacker et al., 2005). Hermann et al. (2006) provides a discussion of the current debate regarding whether the slab fluid is an alkali-chloride aqueous fluid (Keppler, 1996), a silicate melt, or a transitional supercritical liquid (Kessel et al., 2005a). More dilute aqueous solutions (e.g., present at the blueschist to eclogite transition at 60 or so km depths) are regarded as being relatively ineffective in removing trace elements, based

on experimentally derived partitioning data (see Hermann et al., 2006), whereas the silicate melts and supercritical liquids appear more viable as agents for

transfer of slab components into arc source regions and appear to be able to explain the specific enrichments invoked in studies of arc magmatism (see discussion



of sediment melting by George et al., 2005). Based on O-isotope compositions of basalts and basaltic andesites, Eiler et al. (2005) argued for varying contributions of solute-rich aqueous fluid (lower- $\delta^{18}\text{O}$ , from dehydration of hydrothermally altered rocks within the slab) and partial melts of sediments (higher- $\delta^{18}\text{O}$ ) along the Central American volcanic arc (cf. Carr et al., 2003). The work thus far on metamorphic geochemistry in subduction zones has mostly been conducted on suites representing subduction to  $\leq 100$  km in fluid–rock regimes dominantly involving aqueous fluids (Fig. 3). It remains uncertain whether certain element losses from subducting rocks over the full forearc and cross-arc depth range can produce appropriate chemically fractionated residues conveyed into the deeper mantle (Fig. 1), particularly if supercritical liquids or silicate melts become more important agents of transfer from these lithologies during their transit beneath arcs (i.e., at  $> 100$  km depths). Hints of greater LILE depletions in metamorphic suites that experienced partial melting (Becker et al., 2002; Yamamoto et al., 2002; Hacker et al., 2005; LILE data for granulites in Hart and Reid (1991) and a comparison of aqueous-fluid–rock and melt–rock partition coefficients by Kessel et al. (2005a)) are a reminder that we must conduct further geochemical studies on UHP suites on or above wet and dehydration solidi (several candidates for such work included in Fig. 3).

### 5.3. Fluid flow at the subarc slab–mantle interface

There is every reason to believe that the slab–mantle interface is a region of high, but quite heterogeneous, fluid flux — there appears to be no shortage of devolatilization and melting reactions in mafic, sedi-

mentary, and even ultramafic rocks capable of producing large amounts of fluid (aqueous fluid, silicate melt, or supercritical liquid; see Schmidt and Poli, 2003). Relatively coherent tracts of particularly mafic and sedimentary HP and UHP rocks for which limited or no fluid mobility is proposed likely represent the stronger, less permeable lithologies within a lithologic package characterized by strong contrasts in rheology and heterogeneous permeability structure (see Chalot-Prat et al., 2003; Spandler et al., 2003, 2004). Enhanced flux of chemically reactive fluid would tend to produce hydrated, intensely metasomatized assemblages containing minerals such as talc, chlorite, and amphibole that are weak and easily deformed (see Peacock and Hyndman, 1999), thus further enhancing fluid transport. These zones of preferential fluid flow would also be more intensely metasomatized, potentially leading to their disproportionate representation in any aqueous fluid, silicate melt, or supercritical liquid emanating from them into the overlying mantle wedge or upward along the subduction-zone thrust (cf. John et al., 2004; Spandler et al., 2004). Hanging-wall mantle wedge rocks nearest the slab–mantle interface would become hydrated and metasomatically altered, weakening them, leading to their incorporation into the mixing zones (Peacock and Hyndman, 1999; Bebout and Barton, 2002; Breeding et al., 2004; King et al., 2006; Spandler et al., in press). Several groups have presented conceptual models for forearc to subarc processes at/near the slab–mantle interface, based partly on work on sedimentary–mafic–ultramafic metasomatic interactions in mélangé zones (Hermann et al., 2006; Bebout and Barton, 2002; Breeding et al., 2004). Zack et al. (2001) cited recently published mica–fluid partitioning data (Melzer and Wunder, 2001) and, using the Catalina

Fig. 7. Porphyroblast growth and relationship with evolving matrix assemblages, patterned after work by King et al. (2004) and Usui et al. (2006). [sketch (A), and representative SIMS data (B, C), the latter from (King et al., 2004)]. In the garnet porphyroblast shown in (A), the blue and green zones indicate growth within the lawsonite–blueschist and eclogite facies, respectively, thus the garnet growth occurred during, or as a result of, a series of reactions corresponding to the blueschist–eclogite transition (note the different mineral inclusions in the blue and green zones in this garnet). Mineral phases such as lawsonite and clinozoisite have been identified as being particularly important for entraining LREE and Sr deep into subduction zones (Schmidt and Poli, 2003; Feineman et al., 2007), and phengite appears to be extremely important in stabilizing LILE, B, and Li to great depths (see experimental study by Domanik and Holloway, 2002). In (A), note that the garnet contains coesite inclusions only in a region near its rim, perhaps indicating that the rock entered the coesite stability field during the late-stage growth of this garnet (see Kurahashi et al., 2001; King et al., 2004), and that coesite occurs in the matrix within omphacite grains. In (B), a core-to-rim trace element traverse of a garnet in a mafic eclogite from Lago di Cignana, the anomaly indicated by the gray zone was interpreted by King et al. (2004) to reflect the reaction:  $2 \text{ clinozoisite} + 5 \text{ titanite} = 3 \text{ grossular} + 5 \text{ rutile} + 2 \text{ quartz/coesite} + \text{H}_2\text{O}$  (see the similar anomalies presented for garnets in mafic eclogites from the same locality by Lapen et al., 2003). Note the difference in relative enrichments of particularly Gd and Hf, in the garnet on either side of this anomaly, possibly reflecting differing partitioning of these elements between garnet and the changing matrix assemblage. The REE data in (C) demonstrate the depletion of HREE by garnet growth (see data for core and rim), as indicated by HREE zoning in the garnet toward its rim, and by the depletion of HREE in matrix omphacite relative to HREE concentrations in omphacite as inclusions in the garnet. Lithium concentrations are similar for omphacite as inclusions in garnet and as a matrix phase (see D), perhaps consistent with minimal loss of Li during the growth of the garnet and related dehydration. By analyzing such phases as phengite, as inclusions in garnet and as matrix phases, it could be possible to ascertain degrees of isotopic fractionation (e.g., for B and Li) and element loss during segments of prograde  $P$ – $T$  paths (King et al., 2004).

Schist metasedimentary LILE concentrations, suggested that amounts of H<sub>2</sub>O-rich fluid larger than those possible as local dehydration products were required to produce the observed changes in element ratios (particularly Cs/K; discussion in (Bebout et al., 2007)). Those authors suggested that the higher-grade Catalina Schist metasedimentary rocks were flushed by fluids from an external source, leading in particular to the greater Cs loss. Such fluxing of fluids in sedimentary rocks, either underplated to the hanging wall or incorporated as tabular bodies in mélange zones, would be expected if large amounts of fluid ascend from dehydrating mafic and ultramafic rocks at greater depth in the subducting slab section (see Rupke et al., 2004; Tenthorey and Hermann, 2004; Ranero et al., 2005; Peacock et al., 2005).

#### 5.4. Can subduction-zone metamorphism produce precursors for OIB compositional endmembers?

As discussed by Hofmann (2003), it has become relatively routine to associate certain geochemical signatures of the deep mantle (HIMU, EM-1, EM-2, and others) sampled by ocean island basalts, relative to the depleted mantle signature associated with MORB, to varying combinations of variably processed oceanic sediment, oceanic lithosphere, and oceanic island and plateau materials that have conceivably experienced considerable isotopic decay during long-term residence in the deep mantle (see recent discussions by Stracke et al., 2003; Kelley et al., 2005; Stracke et al., 2005; alternative views by McKenzie et al., 2004; Pilet et al., 2005). The HIMU mantle signature is generally regarded as reflecting an igneous crustal precursor, and the EM-type OIB is explained as tracing subducted oceanic crust together with minor amounts of sediment of varying compositions. A number of workers have concluded that, in order to produce precursors to HIMU, it is necessary for subducting AOC to lose large fractions of its Pb and U inventory, relative to Th, then age in the mantle for varying periods of time (Bach et al., 2003; Stracke et al., 2003; Kelley et al., 2005). Bach et al. (2003) concluded that HIMU precursors can be produced from AOC after 1–2 Ga, if ~80–90% Pb, 40–55% Rb, 40% Sr, and 35–40% U are removed during dehydration of these lithologies. This loss, if it occurs beneath arcs, can explain the complementary large enrichments in these elements in arc lavas (Chauvel et al., 1995; Fig. 2A; cf. Kelley et al., 2005). The estimates of the magnitude of these subarc losses largely depend on the starting composition used for the AOC, and the several ODP sites for which AOC sections are well-studied (Sites 801, 504B, 417/418) vary

significantly in their trace element inventories (Fig. 2B). Also, some studies consider a full crustal composite, including gabbro, unaltered basalt, and AOC, as constituting the possible HIMU precursor (see Stracke et al., 2003). A similar relationship exists for the Rb–Sr isotope system, for which significant loss of Rb from AOC is generally invoked in order to produce viable precursor compositions for the HIMU source (Bach et al., 2003; Stracke et al., 2003). In fact, depending on the assumptions employed regarding the composition of the subducting oceanic crust, the Rb, Pb, and U losses that are required represent nearly the full undoing of the Pb–U–Rb enrichment that occurs on the seafloor (see composition of AOC in Fig. 2B), and an oceanic crustal composition unaffected by seafloor alteration, aged to varying degrees in the mantle, appears to more successfully produce the HIMU source composition (see Hauri and Hart, 2003).

The data for Pb, U, Ce, Nb, and Th in HP and UHP rocks presented here indicate that obvious losses of Pb and U, relative to Ce, Nb, and Th, occur in only a small number of HP and UHP metabasaltic and metagabbroic rocks, and it appears that the U (and any possible Pb) enrichments related to seafloor alteration are largely preserved to ~90 km (see Fig. 4C–E). For a number of samples, Pb enrichment appears to have occurred during subduction-zone metamorphism (see John et al., 2004; Fig. 4C). We conclude that, whereas some evidence certainly exists for the mobility of Pb and U in the HP and UHP metamorphic fluids, the Pb–U inventory in AOC is largely retained to these depths, where it could be available for loss beneath arcs.

Hints of increases in Th/U, at relatively constant Th concentration, for some metamafic rocks point to possible U loss in some samples (Fig. 4E). Thorium loss beneath arcs is largely dominated by the subducting sediments, which have far higher Th concentrations than MORB and AOC (see discussions by Plank and Langmuir, 1998; Plank et al., 2002; Plank, 2005; Figs. 2B and 4E). Although relatively few data for Th and U exist for only a few subduction-zone metasedimentary suites, a comparison of metasedimentary Th–Th/U for the Catalina Schist, Franciscan Complex, and Western Baja Terrane with compositions of seafloor sediments (Ben Othman et al., 1989; Plank and Langmuir, 1998) indicates little or no effect of HP metamorphism on these compositions, even in rocks which experienced epidote–amphibolite-facies metamorphism. In the Catalina Schist, only partially melted, amphibolite-facies metasedimentary rocks have Th–Th/U compositions that deviate from the more normal compositions similar to those of seafloor sediment (cf. Plank and Langmuir,



1998), conceivably as the result of removal of low-Th/U “fluids” (aqueous fluids or silicate melts; also see Sorensen et al., 2005). The production of mélange zones, in which coeval metasomatic and mechanical mixing produces hybridized rock compositions, represents another means of decoupling Pb, Th, and U during subduction-zone metamorphism, as has been demonstrated by Breeding et al. (2004) and King et al. (2007).

AOC represents a viable precursor for HIMU OIB sources only if its Rb/Sr is reduced to near its level before hydrothermal alteration on the seafloor, and Sm/Nd would need to be slightly decreased in order for AOC to produce the HIMU compositions (see Stracke et al., 2003). A comparison of the Rb/Sr of AOC with that for the HP and UHP metamafic rocks, many of which had AOC protoliths, demonstrates that this ratio overlaps almost completely with the ratios of their seafloor protoliths (Bebout, in press). The Group IID eclogites of John et al. (2004) show some shift to lower Nd concentrations and higher Sm/Nd, seemingly reflecting loss of LREE relative to MREE, whereas other metabasaltic rocks, including some rinds on blocks in mélange, appear to show Nd enrichment, relative to Sm, producing decrease in Sm/Nd (see Fig. 4F).

Various sediment types are called upon as important precursor lithologies, in addition to oceanic crust, for the EM-1 and EM-2 mantle components (see Eisele et al., 2002; discussions by Hofmann, 2003; Stracke et al., 2003, 2005), to produce the radiogenic isotope patterns, and (particularly for EM-1) contribute to higher Ba ratios to Th, Nb, and La (Weaver, 1991). Barium is very efficiently retained in the metasedimentary suites, and it seems likely that Ba would not be lost appreciably when phengite is present, given its high degree of compatibility in that phase. In the Catalina Schist metasedimentary suite, whole-rock Ba/K is uniform across the wide range of metamorphic grade, as is whole-rock Ba/Th, Ba/Nb, and Ba/La (Bebout et al., 1999, 2007), and similar to that in the Franciscan and Western Baja Terrane metasedimentary rocks (Sadofsky and Bebout, 2003).

As discussed above, the work thus far on metamorphic geochemistry in subduction zones has mostly been conducted on suites representing subduction to  $\leq 100$  km in fluid–rock regimes dominantly involving aqueous fluids (Fig. 3). Thus far, significant whole-rock element loss, even for trace elements thought to be particularly “fluid-mobile” (e.g., B, Cs, and N), has not been documented for these forearc suites, except for metasedimentary units of the Catalina Schist that experienced prograde  $P$ – $T$  paths warmer than those experienced by rocks subducting in Earth’s modern subduction zones (Fig. 5). The jury is out on whether certain element losses

from subducting rocks in the subarc to greater depth range can produce appropriate chemically fractionated residues conveyed into the deeper mantle (Fig. 1), particularly if supercritical liquids or silicate melts derived in sediments and/or oceanic crust become more important agents of transfer from these lithologies during their transit beneath arcs (i.e., at  $> 100$  km depths; see calculated melts and residues for sediment melting by George et al., 2005).

## 6. Final notes

This paper presents a brief synthesis of recent progress in a field in its relative infancy, but with a growing number of researchers entering it, and with some tantalizing initial observations and many hypotheses waiting to be tested. Although the metamorphic record of trench-to-subarc metamorphism is fragmentary, it can complement the work on arc lavas and deep-mantle geochemical heterogeneity in helping identify sources of element and isotope fractionation in subducting slabs and sediment. This work requires sophisticated merging of petrologic and geochemical approaches, as the rocks have experienced protracted prograde and retrograde stages both capable of imparting significant geochemical signatures on these rocks. Future work should exploit microanalytical approaches to extract useful information from rocks with extensive disequilibrium related to complex reaction histories (and kinetics; John and Schenk, 2003), and should partly focus on suites representing subduction to depths of  $> 100$  km that could contain evidence regarding the physical/chemical characteristics of fluids emanating from the slab beneath arcs. This work should consider the consequences of reactive fluid flow along various fluid-flow  $P$ – $T$  trajectories and involving disparate lithologies in the slab, slab–mantle interface, and mantle wedge (Zack and John, 2007). Also highly warranted is a more thorough consideration of the potential geochemical significance of mélange zones generated at the slab–mantle interface, given the apparent ability of mélange formation to generate hybridized chemical and isotopic compositions spanning those of the mafic, sedimentary, and ultramafic end-members generally considered in models of crust–mantle mixing.

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