

3.20

Trace Element and Isotopic Fluxes/ Subducted Slab

G. E. Bebout

Lehigh University, Bethlehem, PA, USA

3.20.1	INTRODUCTION	1
3.20.2	THE SEAFLOOR, AS IT ENTERS THE TRENCHES	4
3.20.3	RECENT THERMAL MODELS OF SUBDUCTION	5
3.20.4	EARLY-STAGE PROCESSING OF SEDIMENTS AND PORE WATERS IN TRENCH AND SHALLOW FOREARC SETTINGS (< 15 km)	5
3.20.4.1	<i>Mineralogical and Compositional Changes During Early Subduction of Sediment</i>	6
3.20.4.2	<i>Records of Fluid and Element Mobility in Modern and Ancient Accretionary Prisms</i>	7
3.20.5	FOREARC TO SUBARC CHEMICAL CHANGES IN HIGH- <i>P/T</i> METAMORPHIC SUITES (15–100 km)	8
3.20.5.1	<i>Lithologies</i>	8
3.20.5.2	<i>Prograde Metamorphic Reactions and Overprinting During Exhumation</i>	10
3.20.5.3	<i>Geochemical Studies of HP and UHP Mafic Rocks</i>	10
3.20.5.3.1	<i>Whole-rock geochemistry of HP and UHP eclogites</i>	12
3.20.5.3.2	<i>Summary and remaining important issues</i>	14
3.20.5.4	<i>Geochemical Studies of HP and UHP Metasedimentary Rocks</i>	17
3.20.5.5	<i>HP and UHP Ultramafic Rocks and Mélange</i>	22
3.20.5.6	<i>Metasomatic Rinds on Blocks in Tectonic Mélange</i>	22
3.20.5.7	<i>Records of Fluid/Element Mobility in Veins, Isotopic Compositions, and Fluid Inclusions</i>	22
3.20.5.8	<i>Prograde Chemical Changes and Open- versus Closed-System Behavior</i>	27
3.20.5.9	<i>Mineral Chemistries of HP and UHP Suites</i>	28
3.20.5.10	<i>Forearc to Subarc: Summary and Outstanding Questions</i>	30
3.20.6	THE DEEP FOREARC AND SUBARC SLAB–MANTLE INTERFACE	31
3.20.7	SLAB-ARC CONNECTIONS	33
3.20.7.1	<i>Brief Discussion of the Geochemistry of Arc Basalts and Inferred Slab Additions</i>	33
3.20.7.2	<i>Cross-Arc Variations</i>	34
3.20.7.2.1	<i>Devolatilization</i>	34
3.20.7.2.2	<i>Boron and lithium isotopes</i>	35
3.20.7.3	<i>Carbon and Nitrogen Input and Arc Output</i>	36
3.20.7.4	<i>Other Stable Isotope Tracers (Oxygen, Hydrogen, and Chlorine)</i>	37
3.20.7.5	<i>The Nature of the Slab-Derived “Fluid” in Arc Magmas</i>	38
3.20.8	BEYOND ARCS	38
3.20.9	SOME FINAL COMMENTS	41
	ACKNOWLEDGMENTS	42
	REFERENCES	42

3.20.1 INTRODUCTION

Subduction zones figure prominently in virtually all chemical geodynamic models of recent and long-term crust–mantle evolution (Allègre, 1989; Zindler and Hart, 1986; Javoy, 1998;

Berner, 1999; Chapter 2.03; also see Bebout, 1995). A thorough understanding of the subduction pathway (see Figure 1) is required to address many aspects of Earth’s large-scale material cycling, including the origin of arc magmas, continental crust formation, and the

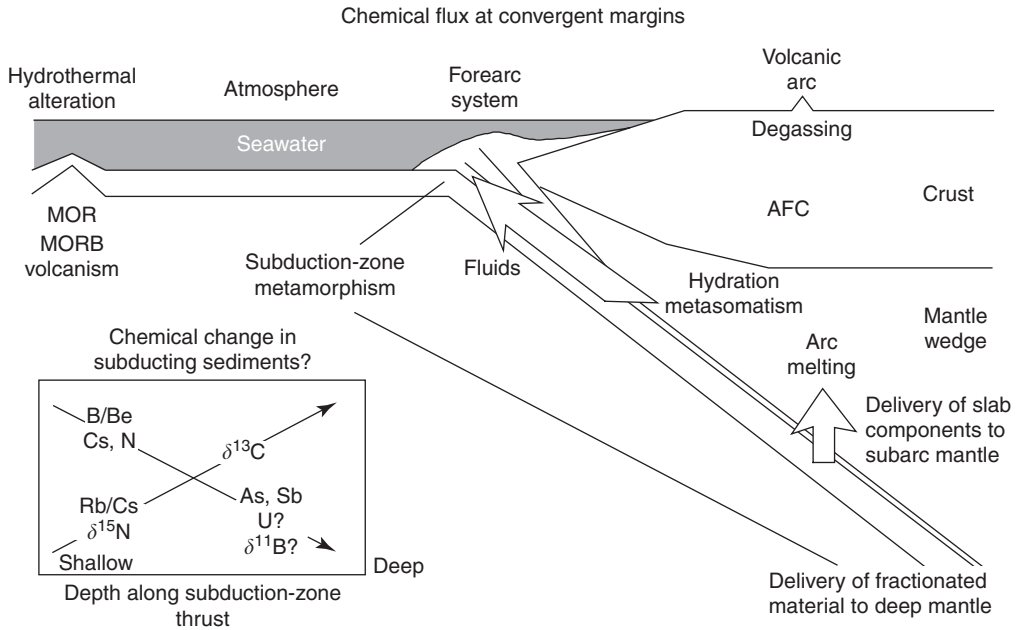


Figure 1 Schematic illustration of a continental margin-type subduction zone, showing possible sites of trace-element and isotopic fractionation. The large arrow along the slab–mantle interface indicates transfer, toward the surface, of volatile components released by subduction-zone metamorphism. Subduction could deliver, to various parts of the mantle (e.g., the forearc mantle wedge, the subarc mantle wedge, and deeper parts of the mantle), C–O–H–S–N fluids, melts, and residual mineral reservoirs strongly fractionated isotopically and chemically relative to initial compositions of the subducted rock reservoir. The inset plot demonstrates the possible evolution of chemical parameters discussed in this chapter with progressive metamorphism of sedimentary rocks during subduction. MOR, mid-ocean ridge; MORB, mid-ocean ridge basalt; AFC, assimilation-fractional crystallization. Reproduced by permission of Elsevier from [Bebout \(1995\)](#).

geochemical evolution of the mantle. Over the last decades, considerable effort has been expended to trace, and even mass balance, elements and isotopes across individual arc-trench systems using seafloor inputs and mostly volcanic arc outputs (e.g., [Plank and Langmuir, 1993](#); [Hilton *et al.*, 2002](#); [George *et al.*, 2005](#); [Li and Bebout, 2005](#); discussion in Chapter 2.11).

Subduction of oceanic lithosphere initiates a complex continuum of diagenetic and metamorphic reactions and related geochemical effects in the down-going slab. For some chemical components, this history profoundly influences the elemental inventory and, in some cases, the isotopic composition of the slab to depths beneath volcanic arcs and beyond. These seafloor lithologies are also subjected to deformation processes that significantly alter their physical state and, in the case of sedimentary accretion and underplating, halt their delivery to depths beyond forearcs. In addition, subduction erosion from the forearc hanging walls can impact geochemical evolution at greater depths (see [Scholl and von Huebner, in press](#)). All of these physical, petrologic, and geochemical processes are thought to vary considerably among Earth’s modern subduction zones (see [Stern, 2002](#)).

Whereas case studies and syntheses of the geochemistry of arc magmas abound (see [Pearce and Peate, 1995](#); [Elliott, 2003](#); Chapter 3.18; [Figure 2a](#)), the study of the geochemistry of slab metamorphic rocks (certain high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic suites) has lagged behind, likely due, in part, to the perceived complexity of the metamorphic field record. In some studies of arc geochemistry, seafloor compositions (“inputs”) are simply compared with arc magmas (the “outputs”), with little or no discussion of the possible effects of subduction-zone chemical processing, whereas in others, specific chemical changes are attributed to metamorphism, providing some exciting and perhaps testable hypotheses. Many studies of HP and UHP metamorphic rocks present cursory geochemical datasets, most commonly major element compositions and concentrations of selected trace elements. However, the number of studies that directly test the influence of metamorphism on the geochemistry of the subducting slab is still surprisingly small.

This chapter provides a synthesis of current knowledge regarding the changes in the physical, petrologic, and geochemical state of subducting oceanic crust that result from diagenesis

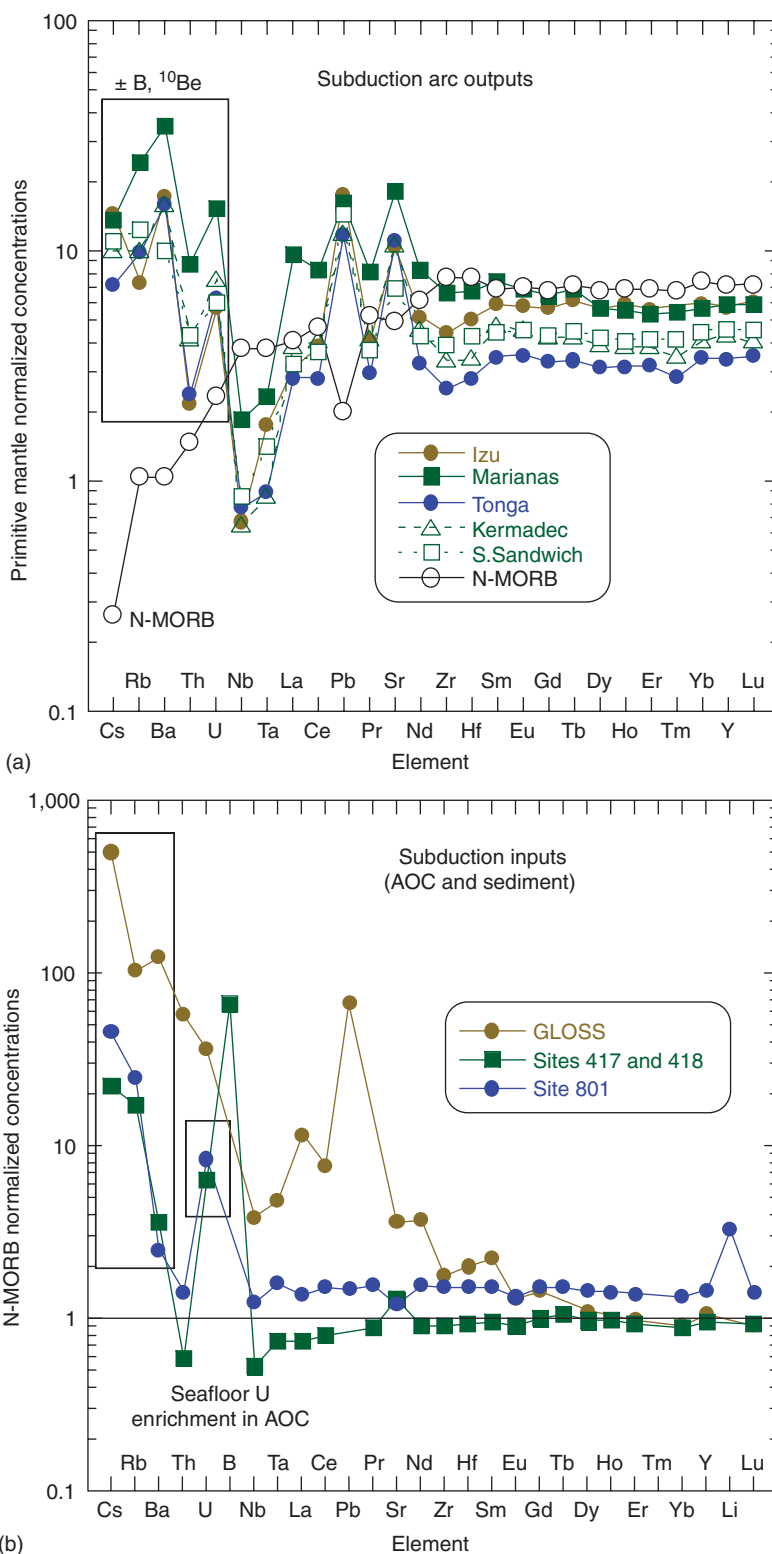


Figure 2 Chemical characteristics of subduction-zone arc outputs, based on erupted basalts (a) and inputs, based on the geochemistry of AOC and sediment (b). Data in (a) and (b) are normalized to primitive mantle and N-MORB, respectively (both from Hofmann, 1988). Data for arc basalt outputs are from Elliott (2003; electronic supplement), the GLOSS (GLOSS composite) is from Plank and Langmuir (1998), and the data for altered oceanic crust at ODP Sites 417/418 and 801 are from Staudigel *et al.* (1996) and Kelley *et al.* (2003), respectively. The boxes in (a) and (b) highlight the similarities in the seafloor enrichments in basalts and the enrichments in arc basalts relative to N-MORB.

and metamorphism along the subduction pathway. The focus in this contribution is largely on the chemical and isotopic tracers commonly employed to elucidate chemical cycling in subduction zones based on study of arc lavas, and on discussion of metamorphic suites for which it is possible to evaluate chemical changes in subducting oceanic crust and overlying sediments (see Chapter 3.09, for discussion of UHP metamorphic geochemistry of continental lithologies in collisional orogens such as Dabieshan-Su-Lu Belt and Kokchetav Massif). Emphasis is placed on elucidating connections between the metamorphic geochemical record and other subduction-related products such as décollement fluids, forearc serpentinite seamounts and mud volcanoes, arc lavas, and deep-mantle geochemical signatures that may result from incorporation of subducted oceanic crust and sediment. For a number of important chemical tracers (e.g., boron, lithium, nitrogen, organic carbon, and nitrogen, perhaps large-ion lithophile elements (LILE), particularly cesium, rubidium, barium, and strontium), significant changes occur during the earliest stages of subduction due to pore water expulsion and diagenesis (and for mafic rocks, possibly hydration). Discussion of the metamorphic record is focused primarily on HP and UHP suites in the circum-Pacific, Cyclades, and European Alps, which have seen the most geochemical study focused on issues of ocean-to-mantle cycling. This review is meant to complement a number of chapters in the *Treatise on Geochemistry*, namely Chapters 2.03, 2.06, 3.09, 3.15, 3.18, and 3.19, and most directly, Chapters 2.11 and 3.17.

3.20.2 THE SEAFLOOR, AS IT ENTERS THE TRENCHES

At first glance, one might consider the subducting oceanic lithosphere to be rather uniform from place to place. On average, it is composed of, a 5–7 km thick section of oceanic crust (see Chapters 3.13, 3.17, and 3.19), dominantly basaltic and gabbroic in composition, with an ultramafic lithospheric mantle section and a sedimentary veneer of varying thickness. However, geochemical data for oceanic crust, either drilled on the seafloor or accessed in on-land ophiolitic sequences, demonstrates a huge diversity of chemical compositions that relate to the nature and duration of fluid–rock interaction on the seafloor (see Alt and Teagle, 2003; Kelley *et al.*, 2003; Staudigel *et al.*, 1996; Chapter 3.15; Figure 2b).

The mid- to lower parts of the oceanic crust are generally thought to have little or no

impact on the slab flux (i.e., the material ascending from the slab to the overlying mantle wedge), as they contain fewer volatile phases and thus do not experience devolatilization reactions and the related fluid mobility necessary for element transport (see Chapter 3.15). However, the extent of hydration in the uppermost mantle of subducting oceanic lithosphere is unclear (see Peacock, 2001; Kerrick, 2002). If such hydration occurs, it could profoundly increase the amount of H₂O being subducted into the deep Earth, possibly causing flux melting of the slab (see Ranero *et al.*, 2005; Kessel *et al.*, 2005), and have great consequences for the deeper geochemistry of subduction zones.

Sedimentary sequences just outboard of trenches have thicknesses ranging from <100 m to >4 km (but mostly <1 km). Factors that influence their chemical compositions (e.g., residence time on the seafloor, water depth, which controls carbonate solubility and deposition, proximity to continental/arc sediment sources, and even ocean currents, which affect organic nutrient budgets) are highly variable. Our knowledge of the lithology and compositions of subducting sediments, largely based on analysis of deep sea drilling program / ocean drilling program (DSDP/ODP) sediment cores, is summarized by Rea and Ruff (1996), Plank and Langmuir (1998), and Jarrard (2003). Plank and Langmuir (1998) discuss the sedimentological, diagenetic, and organic processes dictating the concentrations of major and trace elements of particular interest in chemical-cycling studies (e.g., U–Th–Pb; LILE). Approximately 76 wt.% of the globally subducting sediment (GLOSS) composite of Plank and Langmuir (1998) is composed of “terrigenous” sediment with its largest accumulation near continental margins, and the remainder of this composite consists of calcium carbonate (7 wt.%), opal (10 wt.%), and mineral-bound H₂O (7 wt.%). The GLOSS composite provides an extremely useful guide to the composition of average subducting sediment for use in global chemical mass-balance studies, and Plank and Langmuir (1998) also provide estimates of sediment input into individual modern trenches.

A quick examination of a seafloor bathymetric map reminds us of the large amount of relief on the seafloor, related largely to the presence of ridges and associated transform fault segments, and oceanic plateaus produced by magmatic activity attributed to hotspots. This roughness at the top of the subducting oceanic slab could promote off-scraping/underplating of the areas of higher relief (e.g., ocean–island basalt; Stern, 2002) and representation of these parts of the slab in paleosubduction suites (Maruyama and

Liou, 1989; Cloos, 1993). In many margins, convergence has a significant obliquity, potentially complicating efforts to assess chemical cycling by simple comparison of arc volcanic rocks and offshore subduction sections and, in some margins, the trench sediment section varies significantly along strike of the trench. Transient interactions, such as ridge–trench encounters (e.g., Shervais *et al.*, 2005) might disproportionately affect the tectonometamorphic record of ancient subduction episodes.

3.20.3 RECENT THERMAL MODELS OF SUBDUCTION

A brief discussion of the thermal evolution of subduction zones is appropriate here, as many of the geochemical changes discussed in this chapter occur at the relatively high-pressure/temperature (P – T) conditions in subduction zones. Increasingly high-resolution thermal models, employing variable upper-mantle viscosity and associated subduction-induced “corner flow,” indicate that the slab–mantle interface and shallowest parts of the subducting oceanic crust may be warmer than predicted in earlier models, perhaps at or near temperatures required for partial melting of both sedimentary and mafic rocks (see van Keken *et al.*, 2002; Rupke *et al.*, 2004; Peacock, 2003; Kelemen

et al., 2003; Peacock *et al.*, 2005). As discussed below, this revelation has profound implications for the nature of slab-derived “fluids” and element mobilities. Figure 3 (from Peacock, 2003) presents representative calculated P – T paths for subducting lithologies, demonstrating that these models are highly dependent on the ways in which mantle wedge viscosity is handled (see the discussions by van Keken *et al.*, 2002; Peacock *et al.*, 2005). On a finer scale, Dumitru (1991) matched estimated geothermal gradients for the Franciscan paleoaccretionary margin to thermal models of forearc regions, concluding that the most important variables in these models are the subduction rate, the age of the subducting slab, and frictional heating (see also Peacock, 1992).

3.20.4 EARLY-STAGE PROCESSING OF SEDIMENTS AND PORE WATERS IN TRENCH AND SHALLOW FOREARC SETTINGS (< 15 km)

At shallow levels in subduction zones, complex physical partitioning of sediments and sedimentary rocks into off-scraped, underplated, and more deeply subducted fractions, impacts the sedimentary input contributing to deeper subduction-zone geochemistry. It appears that, in many modern subduction zones,

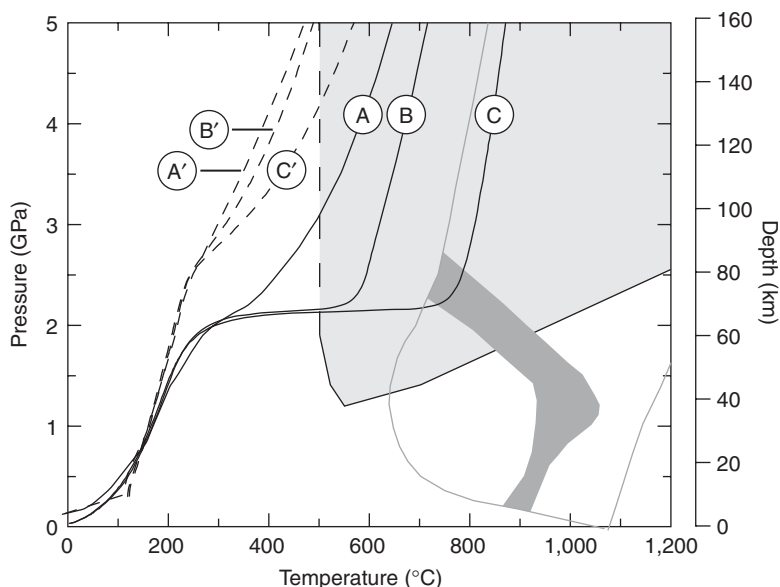


Figure 3 Synthesis of recent thermal models of subduction, incorporating, in different ways, the viscosity in the mantle wedge (figure 6 from Peacock, 2003). The warmest path for the top of the slab (labeled, “C”) is for a mantle wedge having an olivine rheology. Paths “A” and “B,” both also for the top of the slab, correspond to use of isoviscous rheology, at differing model resolution (5 km for “A” and 400 km for “B,” also see van Keken *et al.*, 2002; Peacock *et al.*, 2005). Paths A’, B’, and C’ (broken lines) are for the base of the slab in each corresponding model. The lighter-shaded region is the eclogite-facies stability field, the lighter-shaded, grayish lines are the water-saturated and dry partial melting reactions, and the darker-shaded region is for hornblende dehydration melting (see Peacock, 2003; Chapter 3.17).

sediments are not accreted in the forearc, but rather, subduction erosion may convey large volumes of forearc material of varying lithology to great depths (see Scholl and von Huene, in press). The deep subduction of eroded materials has not yet been adequately considered in geochemical models balancing subduction-zone inputs and outputs. During these earliest stages of subduction, sediments experience large amounts of compaction and deformation, resulting in mechanical expulsion of pore waters (see Moore and Vrolijk, 1992). Sediment porosities of >70 vol.% have been measured outboard of trenches, and for some convergent margins, initial compaction and dewatering produce significant thinning beneath the forearc within a few kilometers of the trench (e.g., the seafloor sedimentary section drilled offshore of the Central American trench (Site 1039) and beneath the forearc wedge (Site 1040) by ODP Leg 170 offshore of Costa Rica; Kimura *et al.*, 1997). Apparently,

this thinning of the sediment section can be accomplished without significant change in many of its trace-element concentrations (see Morris *et al.*, 2002, who presented ^{10}Be data for the young sediment beneath the décollement in the Costa Rica forearc).

3.20.4.1 Mineralogical and Compositional Changes During Early Subduction of Sediment

Reactions among clay minerals (smectite–illite; Srodon, 1999; Brown *et al.*, 2001; Moore *et al.*, 2001; cf. Vrolijk, 1990), particularly those producing low-grade metamorphic micas (see Frey, 1987), result in the release of significant amounts of mineral-bound H_2O (Figure 4) and produce relatively low-chloride fluids in accretionary wedges (see discussions of the influence of reactions among smectite and illite by Kastner *et al.*, 1991, Brown *et al.*, 2001, and

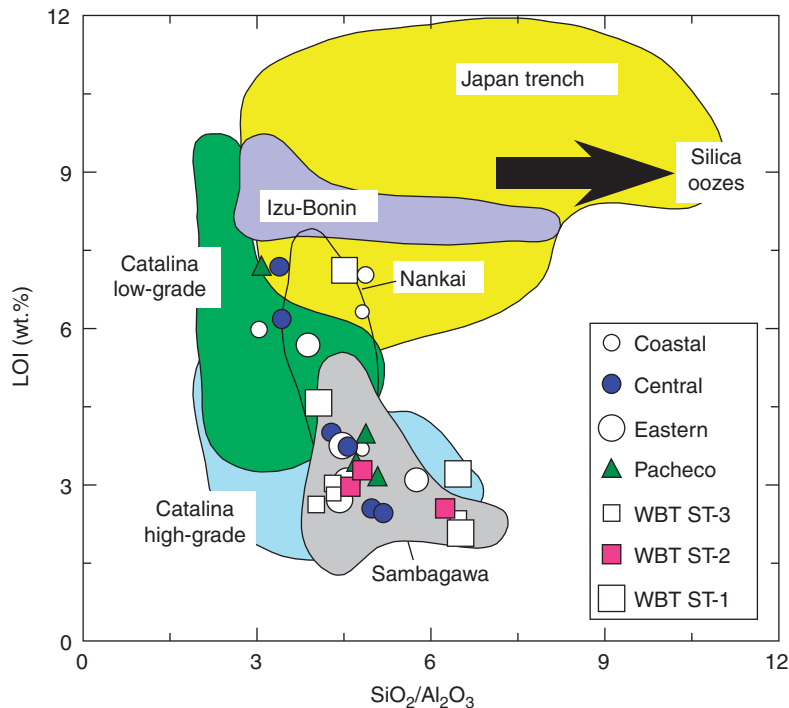


Figure 4 LOI and $\text{SiO}_2/\text{Al}_2\text{O}_3$ for HP paleoaccretionary metasedimentary rocks and their likely seafloor sedimentary equivalents (figure from Sadofsky and Bebout, 2003). Note that LOI correlates with $\text{SiO}_2/\text{Al}_2\text{O}_3$ for the Catalina Schist (data from Bebout *et al.*, 1999), Franciscan Complex Coast Ranges, California (Coastal, Central, and Eastern Belts; data from Sadofsky and Bebout, 2003), Diablo Range, California (Pacheco Pass; data from Sadofsky and Bebout, 2003), Western Baja Terrane (Baja, Mexico; data from Sadofsky and Bebout, 2003), and Sambagawa Belt (Japan; data from Nakano and Nakamura, 2001). Catalina Schist samples are broken down into low-grade facies (lawsonite-albite and lawsonite-blueschist) and high-grade facies (epidote-blueschist, epidote-amphibolite, and amphibolite). Representative marine sediments from the Japan Trench (data from Murdmaa *et al.*, 1980), Nankai trench (data from Pickering *et al.*, 1993), and Izu-Bonin forearc (data from Plank and Langmuir, 1998) are higher in LOI than the metamorphosed sediments, reflecting their higher but varying clay mineral contents. The extremely high-LOI, high- $\text{SiO}_2/\text{Al}_2\text{O}_3$ samples are probably due to dilution of the greywacke signal by pelagic siliceous oozes.

Moore *et al.*, 2001). At shallow levels of accretionary prisms, this metamorphic fluid is likely to be dwarfed by the large amounts of expelled pore waters (see Moore and Vrolijk, 1992); however, the loss of structurally bound H₂O during clay mineral transitions to low-grade micas has important implications for the more deeply subducted H₂O budget dominated by the hydroxyl contents of minerals such as the micas (see Rupke *et al.*, 2002, 2004). Clay minerals also host many of the trace elements of most interest to those studying arc lava “slab additions” (boron, lithium, nitrogen, rubidium, cesium, and barium; see discussion below of sediment versus metasedimentary Rb/Cs). Illite, in particular, is an initial primary host for LILE such as cesium, barium, and rubidium, and for nitrogen and boron (for discussion of the incorporation of organic nitrogen and boron into diagenetic illite, see Compton *et al.*, 1992 and Williams *et al.*, 2001, respectively). Other dehydration reactions in shallow parts of accretionary prisms include the transformation of opal-A (which contains ~11 wt.% H₂O) to opal-CT (opal which shows the beginning of formation of domains of short-range ordering) to quartz (Moore and Vrolijk, 1992) as siliceous microfossil skeletons recrystallize. The smectite–illite and opal–quartz transformations occur over a temperature range of ~60–160 °C, depending on heating rates (Moore and Vrolijk, 1992).

Shallow reactions involving organic matter appear to be responsible for the release of large amounts of methane (biogenic methane and methane produce abiologically by heating) in many forearcs (see Moore and Vrolijk, 1992). However, the similarity in the reduced (organic) C concentrations and isotopic compositions (and C/N ratios) between sediments outboard of trenches and those in forearc metasedimentary rocks (representing subduction to 5 km or more) indicates small amounts of loss of reduced C over large volumes of sediment to produce the methane that is observed to seep out along structures. Diagenetic conversion of organic nitrogen into ammonium in clay minerals, such as illite, begins on the seafloor (see Sadofsky and Bebout, 2004a; Li and Bebout, 2005) and probably continues during very shallow subduction. This transfer of organic nitrogen into clays, and then into low-grade micas, appears to be remarkably efficient, as the C/N and nitrogen concentrations and isotopic compositions in forearc metasedimentary rocks subducted to depths of up to ~40 km are similar to those in their seafloor sediment protoliths (see Bebout, 1995; Sadofsky and Bebout, 2003).

Small amounts (<5 wt.%) of finely disseminated calcite occur in metasedimentary rocks in

the Coastal Belt of the Franciscan Complex, California (representing sediments underthrust to ≤5 km depths; see Blake *et al.*, 1987), but are absent in somewhat higher-grade units representing subduction to up to 30 km (Sadofsky and Bebout, 2003). This difference could have resulted from minor decarbonation or dissolution of calcite in aqueous fluids, producing not only a decrease in CO₂ content, but also decreases in whole-rock CaO and strontium. Moreover, loosely adsorbed boron, with relatively high-δ¹¹B, is believed to be lost during early-stage mineral reactions and pore water expulsion, resulting in a decrease in whole-rock δ¹¹B of subducting sediments (see discussion by Bebout and Nakamura, 2003). Sadofsky and Bebout (2003) argued for a similar loss of small amounts of nitrogen with relatively high δ¹⁵N to mechanically expelled pore waters at low grades in the Franciscan Complex and suggested that this was more loosely adsorbed nitrogen, perhaps occurring as nitrate.

3.20.4.2 Records of Fluid and Element Mobility in Modern and Ancient Accretionary Prisms

There is a wealth of geochemical data for pore fluids in accretionary prism sediments and more deformed zones, including décollement. These provide a record of element mobilization, in some cases related to reactions of the types discussed above that produce low-salinity waters, which locally dilute the more saline pore waters (Elderfield *et al.*, 1990; Kastner *et al.*, 1991; Moore and Vrolijk, 1992; also see discussions of forearc mud volcanoes in You *et al.*, 2004; Godon *et al.*, 2004). In addition to the dehydration or breakdown of clay minerals and opal-A (amorphous opal), influences on pore water chlorinity include the dissociation of methane gas hydrates (clathrates; see Kvenvolden, 1993), clay membrane ion filtration, biogenic or thermogenic combustion of organic matter, dissolution of minerals, mixing of fluids from different sources, and decarbonation reactions and related reduction in CO₂ content. Fluids sampled in the décollement on ODP drilling legs commonly have decreased chlorinity, variable ⁸⁷Sr/⁸⁶Sr, δ¹⁸O, and Sr concentration, increased methane, silica content, and Mg²⁺/Ca²⁺, and decreased Ca²⁺ content relative to fluids away from such structures (Kastner *et al.*, 1991; cf. Elderfield *et al.*, 1990; for discussion of trace elements in pore waters in and away from décollement see Zheng and Kastner, 1997). Solomon *et al.* (2006) documented liberation of barium from barite at shallow levels beneath the décollement in the

Costa Rica forearc (ODP Site 1040), and discussed the possible implications of this barium release for deeper subduction barium cycling. During the earliest stages of subduction, a large fraction of the sediment barium inventory can be tied up in the sulfate mineral barite, and sulfate depletion releases this fraction leaving only the barium component contained in the silicate and carbonate fractions of the sediment.

Vein networks in exposures of paleoaccretionary rocks formed at <15 km depths record large-scale fluid-mediated mass (and heat) transfer, and more specifically, document the mobility of methane-bearing, low-chlorinity, H₂O-rich fluids (see Moore and Vrolijk, 1992; Fisher, 1996). The methane is considered to be thermo- or biogenic in origin, and these sources can be distinguished on the basis of C isotope signatures (Ritger *et al.*, 1987). The specifics of vein formation, and the origin of the vein minerals (generally quartz- and/or calcite-rich), for example, introduced via advection of mineral components or diffusion into fractures from nearby host rocks, are debated for individual cases (see Fisher, 1996). Nevertheless, extensive vein networks are generally considered to reflect upward migration of fluids generated by a combination of compaction and dehydration of more deeply buried sediments (see Sadofsky and Bebout, 2004b). This is supported by the relatively lower salinities and elevated methane concentrations in fluid inclusions within vein minerals (e.g., Vrolijk *et al.*, 1988), evidence consistent with the “freshening” observed in faults and décollement at shallower levels (Brown *et al.*, 2001; Moore *et al.*, 2001). Based partly on the strontium-isotope compositions of veins, Sample and Reid (1998) argued that some of the fluids originate in the subducting slab (cf. Breeding and Ague, 2002).

Serpentinite seamonts in the Marianas margin are produced by the release of fluids from subducting sediments and altered oceanic crust (AOC) in shallow parts of the forearc and the reaction of these fluids with the forearc ultramafic mantle wedge. In addition, mafic blueschist-facies clasts in these settings provide a confirmation of the *P–T* estimates from thermal models of the modern Marianas slab interface (see Maekawa *et al.*, 1993), and a glimpse at the subducting oceanic crust from these depths in the forearc that complements the field record of mafic rocks in paleoaccretionary complexes such as the Franciscan Complex. Studies examining the major and trace-element and isotopic compositions of these serpentinite muds (and ultramafic clasts contained therein) in these seamonts have attempted to estimate the compositions of the fluids that generated the serpentinite at depth

and have invoked additions of trace elements such as boron, lithium, arsenic, and cesium to these fluids from subducting oceanic crust and sediment (see Ryan *et al.*, 1996; Benton *et al.*, 2001, 2004; Savov *et al.*, 2005). One series of seamonts in the Marianas forearc allows an estimate of progressive fluid and element loss as a function of distance from the trench (depth to the slab; Mottl *et al.*, 2004) and provides a link with studies of devolatilization and fluid flow in paleoaccretionary complexes derived from these same depths. Mottl *et al.* (2004) interpreted trends in pore water Na/Cl, B, Cs, and especially K and Rb, across this suite of seamonts (Figure 5) as reflecting their derivation from the top of the subducting plate, driven by increasing temperature, and suggested that the trends reflect dominantly upward flow with minimal lateral mixing. The range of depth inferred for the top of the slab beneath these seamonts (16–29 km) falls within the depth ranges estimate for peak metamorphism of the Franciscan Complex, Western Baja Terrane, and Catalina Schist, for which the chemical effects of metasedimentary devolatilization have been determined (Bebout *et al.*, 1993, 1999; Sadofsky and Bebout, 2003). The mobility of the elements deduced from these studies is compatible with the results of sediment-fluid experiments of You *et al.* (1996), indicating enhanced mobility of boron, NH₄, arsenic, beryllium, cesium, lithium, lead, and rubidium in forearc fluids. However, Bebout *et al.* (1999) and Sadofsky and Bebout (2003) demonstrated that, in cool subduction zones represented by most of the forearc metasedimentary suites, these fluid-mobile elements (boron, cesium, arsenic, and antimony) are largely retained in metasedimentary rocks subducted to depths of up to 40 km at concentration levels similar to those in seafloor sediments. Thus, it appears that, as for organic carbon and nitrogen, the mobility of these elements at shallower levels represents a relatively small proportion of the inventory found in sediment in some forearcs.

3.20.5 FOREARC TO SUBARC CHEMICAL CHANGES IN HIGH-*P/T* METAMORPHIC SUITES (15–100 km)

3.20.5.1 Lithologies

Subduction zone HP to UHP metamorphic suites contain a potpourri of variably metamorphosed mafic rocks crudely corresponding in chemical composition to altered seafloor basalt and gabbro and, in many cases, even preserving pillow and other fabrics indicative of

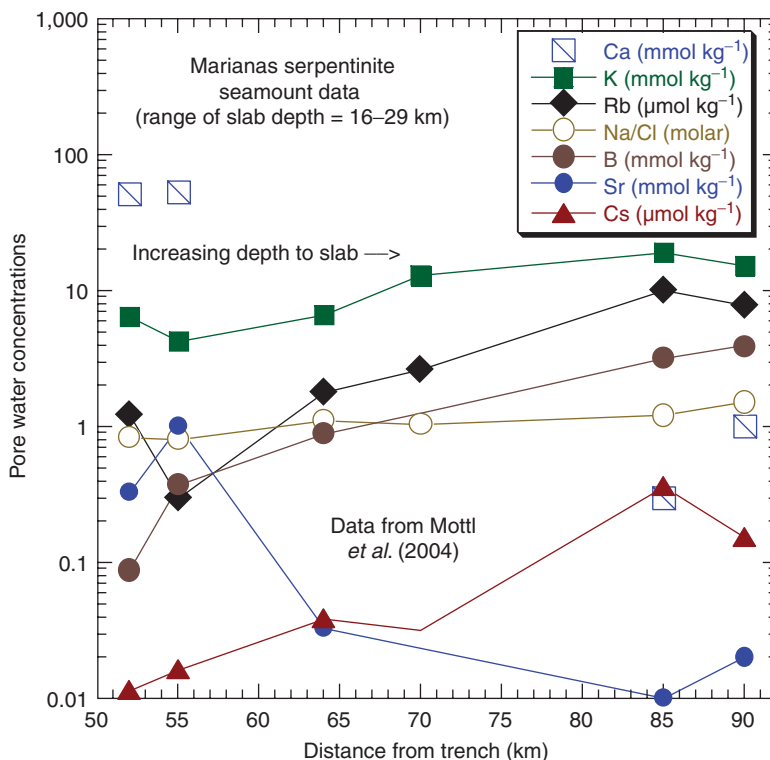


Figure 5 Variations in pore water chemistry in Marianas forearc serpentinites, as a function of distance from the trench, thought to represent progressive element loss from the subducting slab at 16–29 km depths. A number of compatibilities exist between these data and the data for paleoaccretionary rocks in the Catalina Schist and Franciscan Complex (both in California), Western Baja Terrane (Baja, Mexico), and Sambagawa (Japan), including the evidence for Sr loss at shallow levels, and increasing metamorphic losses of B, Rb, and Cs with increasing depth in the forearc. Vein geochemistry and, for B and Sr, whole-rock trends demonstrate the mobility of these elements in the forearc metasedimentary suites representing 5–30 km (see [Bebout *et al.*, 1999](#); [Nakano and Nakamura, 2001](#); [Sadofsky and Bebout, 2003](#)). Data from [Mottl *et al.* \(2004\)](#).

submarine extrusion ([Barnicoat, 1988](#); [Kullerud *et al.*, 1990](#)). The structural setting of these rocks varies widely from exposure in relatively intact ophiolitic sequences, such as in the Tethyan ophiolites in the Western Alps, to occurrences as blocks of meter to kilometer sizes occurring within mélangé with large sedimentary and/or ultramafic components (such as in the Franciscan, Japan, the Cyclades, northern Turkey, Sulawesi, and New Caledonia; see [Moore, 1984](#); [Cloos, 1986](#); [Dixon and Ridley, 1987](#); [Sorensen and Barton, 1987](#); [Bebout and Barton, 1993](#); [Okamura, 1991](#); [Parkinson, 1996](#); [Breeding *et al.*, 2004](#); [Altherr *et al.*, 2004](#); [Spandler *et al.*, 2004](#)). Whereas some of the mafic rocks appear to have derived, at least in part, from gabbroic protoliths developed in “Atlantic-type” seafloor systems such as those exposed in the Alps (see [Tricart and Lemoine, 1991](#); [Chalot-Prat, 2005](#)), the more dismembered tectonic blocks in circum-Pacific complexes are generally metabasaltic, with mid-ocean ridge basalt (MORB)-like or, to a lesser extent, island-arc basalt (IAB)-, or ocean-island basalt (OIB)- like chemical characteristics. These

tectonic blocks are commonly rimmed by what are interpreted as being metasomatic rinds, representing chemical interactions between the blocks, their metasedimentary or ultramafic surroundings, and metamorphic fluids (e.g., [Moore, 1984](#); [Sorensen and Grossman, 1989, 1993](#); [Sorensen *et al.*, 1997](#); [Breeding *et al.*, 2004](#); [Altherr *et al.*, 2004](#)). Some low-grade metasedimentary mélangés contain mafic blocks showing a range of peak metamorphic grade (see [Cloos, 1986](#)). Thus, the blocks and mélangé matrix cannot be assumed to have achieved peak metamorphism at the same pressure and temperature conditions. Metabasaltic blocks can also occur within quartzofeldspathic gneiss or marble (e.g., Trescolmen, Adula Nappe, [Zack *et al.*, 2002](#); for discussion of suites representing subduction of continental crust, such as the Dabieshan-Su-Lu Belt, see [Li *et al.*, 2000](#); Chapter 3.09). Given the wide range of textural settings and presumed origins of the mafic rocks in HP and UHP metamorphic suites, and the huge range in chemical compositions of these lithologies and their presumed seafloor protoliths, it can be difficult to identify

chemical change that is unequivocally related to prograde subduction history. Furthermore, for the tectonic blocks floating in a chemically disparate mélangé matrix with which they have metasomatically exchanged, it can be difficult to infer geochemical evolution in coherent oceanic crustal slabs experiencing prograde metamorphism in subduction zones. Less attention has been paid to the study of subduction-related chemical alteration in the UHP mafic eclogites in the Dabieshan-Su-Lu Belt and Kokchetav Massif representing deep subduction of more continental lithological packages. However, Yamamoto *et al.* (2002) provide a preliminary analysis of element loss in Kokchetav rocks that were metamorphosed at ≤ 6.0 GPa and 950 °C. Generally, the eclogites in these terranes are regarded as being more “continental,” not obviously having had MORB protoliths (see Jahn, 1999, Chapter 3.09). It is possible that detailed study of the prograde chemical evolution (evolution during the increases in pressure and temperature related to underthrusting) of these eclogites will provide insights into the evolution of similar lithologies subducted in ocean–ocean settings.

Largely metasedimentary paleoaccretionary complexes, such as those in the circum-Pacific, probably do not sample the lower, more pelagic part of the sediment sections (deposited in the deep sea far from the trench, at relatively low sedimentation rates), thus biasing the field record relative to what is/was more deeply subducted. Instead, these complexes are dominantly terrigenous sediment derived from arcs and continental crust that were deposited into the trench (see Sadofsky and Bebout, 2004b). In some forearcs, sediment sections below the décollement have been drilled (e.g., ODP Site 1040; Kimura *et al.*, 1997; Morris *et al.*, 2002), providing information on the earliest diagenetic processes that occur as pelagic sediments enter subduction zones. In more coherent exposures (not obviously representing tectonic blocks in mélangé) of HP and UHP metaophiolite exhumed during initial collision (e.g., the Jurassic ophiolites of the Western Alps; see Jolivet *et al.*, 2003), it is possible to identify related seafloor sediment. One example is the siliceous and Mn- and carbonate-rich metasediment in contact with the Jurassic ophiolite at the UHP Lago di Cignana locality (see Reinecke, 1998).

3.20.5.2 Prograde Metamorphic Reactions and Overprinting During Exhumation

Both continuous and discontinuous metamorphic reactions occur along P – T paths

traversing the lawsonite–blueschist, epidote–blueschist and eclogite facies. It is not possible to do justice to this topic in this chapter; however, Chapter 3.17 provides an excellent synthesis of the field, experimental, and theoretical constraints on prograde metamorphic reaction history in subducting mafic and sedimentary lithologies. Several recent studies calculated phase equilibria in KFMASH and NKFMASH for HP and UHP metapelitic rocks (see Proyer, 2003; Wei and Powell, 2004; also see Liou *et al.*, 1987; El-Shazly and Liou, 1991), and Proyer (2003), in particular, considered the extent of exhumation-related reaction expected for various metapelitic bulk compositions.

Interpreting each HP and UHP suite in terms of subduction history carries with it its own challenges associated with tectonic and lithologic complexity. One key factor when selecting suites best suited for geochemical work is the thermal history that the rocks experienced during exhumation (see the P – T diagram in Figure 6). Extents of exhumation-related overprinting are, in general, related to the degrees of heating during decompression, the duration of any heating (or cooling) during this decompression, the volatile content of the rocks prior to exhumation, and the bulk composition of the rocks. The latter dictates whether or not certain decompression-related reactions occur (see Proyer, 2003). The greatest prospects for survival of prograde reactions and geochemistry are found in mafic rocks that experienced relatively rapid, down- T exhumation paths. Such paths are commonly attributed to exhumation during continued, active underthrusting to explain the sustained high- P – T conditions. For a number of HP and UHP suites, metasedimentary rocks experience far greater overprinting during exhumation than adjacent metabasaltic rocks (Reinecke, 1998; van der Klauw *et al.*, 1997; Fitzherbert *et al.*, 2005). This is because the metasedimentary rocks show greater pervasive deformation and open-system behavior than the metabasalts and experience different decompression-related mineral reaction histories. Miller *et al.* (2002) (also see van der Klauw *et al.*, 1997) provide a summary of fluid processes associated with the exhumation of HP and UHP metamorphic rocks.

3.20.5.3 Geochemical Studies of HP and UHP Mafic Rocks

A number of subduction-zone processes could influence the compositions of subduction zone HP and UHP mafic lithologies relative to those

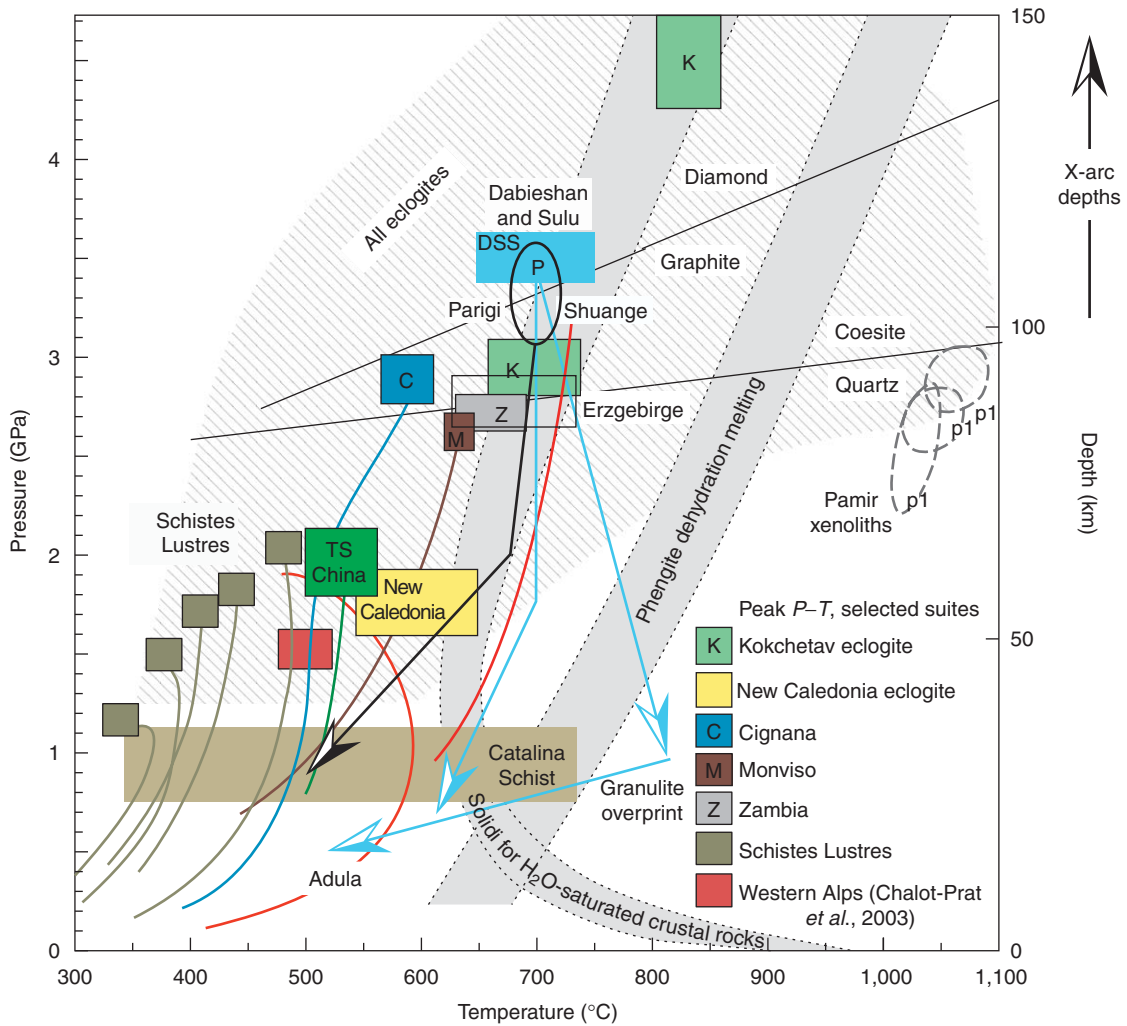


Figure 6 The peak P – T conditions for metamorphic suites discussed in this chapter, some representative exhumation P – T paths, the positions of the wet and dehydration solidi for partial melting of mafic and sedimentary lithologies, and peak metamorphic conditions of some other selected UHP suites (figure modified after Hacker, *in press*; also note the patterned field for “All eclogites,” and the graphite–diamond and quartz–coesite equilibria). Colored rectangles are peak P – T conditions of the suites discussed in this chapter (mostly from Hacker, *in press*; references for peak P – T estimates provided therein; p, Pamir in dashed-oval regions; see Hacker *et al.*, 2005, for discussion of these partially melted metasedimentary rocks). For the Schistes Lustres, the multiple fields are for individual units showing a wide range in grade (from Agard *et al.*, 2002; see data for these units in Figure 12), and an estimated exhumation path is shown for each. Schematic exhumation paths for the Dabie-Sulu UHP rocks (light blue, straight-line segments) are from Zheng *et al.* (2003); also see P – T path for the Shuangge UHP locality in Dabie. Figure 9 provides greater detail regarding the peak P – T and varying prograde P – T paths of the units of the Catalina Schist. The P – T for the Western Alps is for the internal units (see Chalot-Prat *et al.*, 2003), and peak metamorphic P – T estimates for Tianshan HP rocks are from Gao and Klemd (2001). The black, unfilled oval region is for the Parigi UHP locality of the Dora Maira Massif (see discussion in Hermann *et al.*, *in press*; Sharp *et al.*, 1993), and the black, unfilled rectangular region is for the Erzgebirge UHP rocks studied by Massone and Kopp (2005). The Adula rocks (exhumation path only) were investigated by Zack *et al.* (2001, 2002, 2003).

of AOC drilled some distance from the trench (e.g., Sites 801, 1149, 504B; see Chapter 3.15). These include hydration and metasomatism related to plate bending in the trench (see the discussion by Ranero *et al.*, 2005), volume strain (involving selective element removal; see Bebout and Barton, 2002), devolatilization

and other fluid–rock interactions along the slab–mantle interface (including interaction with sediment-derived fluids, development of metasomatic rinds on tectonic blocks), and for the higher grade lithologies, extraction of partial melts. Recent work that has attempted to identify chemical signatures of subduction-zone

metamorphism in HP and UHP metabasaltic and metagabbroic rocks, and the chemical contributions of subducted oceanic crust to arc source regions and the deeper mantle, is briefly mentioned here. Slab additions to the mantle wedge beneath arcs are generally presumed to occur via a “fluid” phase, variably described as being hydrous fluid, silicate melt, or supercritical liquid (see [Kessel *et al.*, 2005](#), and references therein). Study of the geochemistry of subduction zone HP and UHP mafic rocks thus provides insight into slab fluid production and mobility, and possible element loss in these fluids.

3.20.5.3.1 Whole-rock geochemistry of HP and UHP eclogites

One of the largest obstacles to demonstrating chemical fluxes in subduction-related metabasalts, relative to their protoliths, is the need to identify variations caused by either magmatism or seafloor alteration (see Chapters 2.03 and 3.15). Generally, the first step in geochemical studies of mafic HP and UHP metamorphic rocks is to compare the major and trace-element compositions of these rocks to those of seafloor basalts. This is done with varying rigor, involving comparisons of the compositions of the HP/UHP rocks with compositions of both fresh normal MORB (N-MORB) and enriched MORB (E-MORB), various AOC composites, and other estimates. In most studies, the metamorphic rocks are deemed to be derived from seafloor basaltic or gabbroic rocks, but in some cases either OIB or IAB protoliths are considered ([Becker *et al.*, 2000](#); [John *et al.*, 2004](#); [Saha *et al.*, 2005](#); [Usui *et al.*, 2006](#)). The more sophisticated approaches involve comparison of the variation among samples in a suite with the variation expected for magmatic differentiation beneath spreading centers (e.g., [Chalot-Prat *et al.*, 2003](#); [Spandler *et al.*, 2004](#); [John *et al.*, 2004](#)). In the Western Alps, it is possible to examine relatively coherent tracts of Jurassic ophiolites that experienced a wide range of metamorphic grade, from very low-grade external nappes that “escaped subduction” (see [Chalot-Prat, 2005](#)) to the internal nappes that experienced up to eclogite-facies metamorphic conditions ([Chalot-Prat *et al.*, 2003](#); [van der Klauw *et al.*, 1997](#)).

The suites that have been studied in detail, and for which data are compiled in this section, occur in very different structural–textural settings (e.g., as tectonic blocks, closely juxtaposed with *mélange* matrix lithologies with which they have interacted, or as more coherent and larger tracts of identifiably oceanic crustal lithologies).

Fluid–rock interaction, and associated metasomatism during subduction-zone metamorphism, is expected to differ dramatically for rocks from these different settings. For the mafic blocks in *mélange*, it is difficult to establish the relationship between the blocks in time, space, and composition, and comparisons with protoliths are necessarily less direct ([Sorensen *et al.*, 1997](#)). In such cases, one is often concentrating on characterizing metasomatic additions (e.g., LILE) resulting from block–matrix–fluid exchange (see [Sorensen and Grossman, 1989, 1993](#); [Nelson, 1995](#); [Bebout and Barton, 2002](#); [Saha *et al.*, 2005](#)) and, to a lesser extent, the possibility of element depletions related to devolatilization. Nonetheless, blocks investigated in these studies generally show geochemical affinities with MOR basalts (see [figure 3](#) in [Sorensen *et al.*, 1997](#)), and occasionally OIB or IAB (see [MacPherson *et al.*, 1990](#); [Saha *et al.*, 2005](#)). The evidence for element enrichments in these blocks and their metasomatic rinds provides an extremely valuable record of the mobilities of volatiles (e.g., H₂O) and major and trace elements in the HP and UHP metamorphic fluids (see [Sorensen *et al.*, 1997](#)).

In general, the HP and UHP mafic rocks scatter about average N-MORB concentrations for many moderately to highly compatible trace elements (one exception is lithium), but show large enrichments in many of the trace elements that are highly incompatible during mantle melting (cesium, rubidium, barium, uranium, thorium, lead, strontium, and potassium; the “highly nonconservative” elements of [Pearce and Peate, 1995](#)). In this way, the mafic HP and UHP rocks resemble various AOC composites ([Staudigel *et al.*, 1996](#); [Kelley *et al.*, 2003](#); see [figure 7](#) in [Bebout, 1995](#)). Enrichments of these same highly incompatible trace elements in arc lavas are attributed to additions from slab-derived fluids (see [Pearce and Peate, 1995](#); [Elliott, 2003](#)), and are the focus of the compilations and discussion in this section.

Ratios of some LILE have the potential for distinguishing between the effects of seafloor hydrothermal alteration and fluid–rock interactions during subduction-zone metamorphism (see discussion of LILE mobility by [Zack *et al.*, 2001](#); [Figure 7](#)). [Zack *et al.* \(2001\)](#) suggested that it might be necessary for eclogites to be infiltrated by fluids from external sources in order to produce LILE depletions dramatic enough to be demonstrable given the protolith variability issue (see [Bebout *et al.*, in press](#), and discussion below of how this argument pertains to metasedimentary rocks in the Catalina Schist). However, [Figure 7a](#) shows that, for the HP and UHP suites that have been studied in detail, the enrichments of potassium and rubidium due to seafloor alteration are difficult

to distinguish from those due to subduction enrichments or depletions (a similar relationship exists for cesium enrichments). Any addition or subtraction of potassium, rubidium, and cesium due to the passage of fluids during HP/UHP metamorphism is obscured by this overlap with the trends for seafloor alteration. In contrast, barium is generally not as enriched as potassium, rubidium, and cesium during seafloor hydrothermal alteration (see Staudigel *et al.*, 1996; Kelley *et al.*, 2003; Chapter 3.15; see Figure 2a), yet many metabasaltic rocks in HP suites have high barium concentrations. In some cases these enrichments have been attributed to HP metasomatic additions by fluids having previously interacted with sedimentary lithologies (see Sorensen *et al.*, 1997; compilation of Catalina Schist metabasaltic data in figure 7 of Bebout, 1995). Figure 7b shows relationships between potassium and barium (here normalized to thorium, which shows enrichment in some samples; see Figure 8d) indicating that enrichments due to hydrothermal alteration on the seafloor can be distinguished from those that occur during subduction-zone metamorphism. In these plots, some HP and UHP metamorphic samples show ratios of potassium and barium concentrations to thorium concentrations lower than those of fresh and altered MORB (and even OIB, see figure 4b in Becker *et al.*, 2000), perhaps indicating loss of potassium and barium from some samples, relative to thorium, during subduction-zone metamorphism (see Becker *et al.*, 2000; Spandler *et al.*, 2004). Becker *et al.* (2000) also noted lower potassium contents in subduction-zone metabasalts relative to seafloor basalts with similar elevation in $^{87}\text{Sr}/^{86}\text{Sr}$ attributed to seafloor alteration, and concluded that this relationship represents potassium loss. Figure 7c provides another view of the barium–potassium enrichments (and possible losses in a smaller number of samples), incorporating rubidium concentrations, and demonstrates trends of metasomatic addition (most prominently displayed by the rind data), seafloor alteration, and Rayleigh loss to dehydration fluids (the latter trends calculated by Zack *et al.*, 2001, using recently published fluid–mica partition coefficients by Melzer and Wunder, 2001). Based on a more complete consideration of the heterogeneity of oceanic crust protoliths, a consensus has recently developed that the HP and UHP metamorphic loss of elements such as barium, potassium, and uranium from such rocks is generally relatively restricted, but that significant localized losses can occur in zones of concentrated fluid–rock interaction (see Bebout and Barton, 2002; Chalot-Prat *et al.*, 2003; Spandler *et al.*, 2004, John *et al.*, 2004).

Extensive enrichment of uranium during seafloor hydrothermal alteration of oceanic crust (see Staudigel *et al.*, 1996; Kelley *et al.*, 2003) causes large fractionations of uranium from other trace elements of similar incompatibility during mantle melting (thorium, niobium, cerium, and lead). Fluxes of these elements in subduction zones are of particular interest in studies of arc lavas and deep-mantle geochemical heterogeneity (see Section 3.20.8). In particular, large fluxes of uranium and lead, off the slab, are invoked to explain the elevated concentrations of these elements in arc lavas. Figures 8a and 8b illustrate the relationships among cerium and lead concentrations for MORB and OIB, variably altered seafloor basalt, and selected HP and UHP metabasaltic and metagabbroic suites. Several metasomatic rinds developed on Franciscan mafic blocks (see Saha *et al.*, 2005), and one group of eclogites for which John *et al.* (2004) invoked enhanced fluid–rock interaction (their Group IID eclogites), show some decrease in Ce concentration and associated reduction in Ce/Pb (Figure 8a). John *et al.* (2004) proposed that some combination of seafloor alteration, subduction-zone fluid–rock interactions, and possibly also exhumation effects, produced significant lead enrichment (see the trends toward the origin at low 1/Pb, one for the Group IID eclogites), and related decreased Ce/Pb in the UHP eclogites from Zambia (Figure 8b). This correlated Pb enrichment and decrease in Ce/Pb is noted for only a small number of samples of seafloor-altered basalt (possibly some samples from ODP Site 1149), and for low-grade metamorphosed seafloor basaltic rocks from the external units in the Alps (studied by Chalot-Prat, 2005, and not directly representative of seafloor altered basalt), perhaps indicating that the Pb enrichment documented by John *et al.* (2004) resulted from subduction-zone metamorphism (or postpeak metamorphic fluid–rock interactions).

The trend of uranium enrichment of AOC can be seen in Figure 8c (also see the data for AOC in this figure). A decrease in Nb/U is also observed in nearly all of the HP and UHP eclogites. Very few of the metamafic rocks contain lower uranium concentrations or higher Nb/U than that found in AOC, and it is likely that extreme loss due to metamorphism would be necessary to discern a metamorphic effect. In addition, the Th/U of AOC will be lowered due to hydrothermal alteration (see Staudigel *et al.*, 1996). Figure 8d compares Th/U of fresh MORB, AOC and seafloor sediment, and some representative metamorphic data. A number of the metamafic samples have higher Th/U than that of AOC and MORB, perhaps due to

uranium loss (see the data for the Group IID eclogites of [John *et al.*, 2004](#)). Interestingly, high-grade Catalina Schist metasedimentary rocks (amphibolite facies) have Th/U higher than that of their lower-grade equivalents (in the Catalina Schist and in the Franciscan Complex and Western Baja), likely related to uranium loss with or without some thorium enrichment during partial melting reactions (see [Figure 8d](#); [Bebout *et al.*, 1999](#)). Studies of HP mélanges have demonstrated decoupling of thorium and uranium by combinations of metasomatic and mechanical mixing (see [Breeding *et al.*, 2004](#); [King *et al.*, 2006](#); see below), and it is possible that these processes cause significant fractionation of these elements at depth in subduction zones.

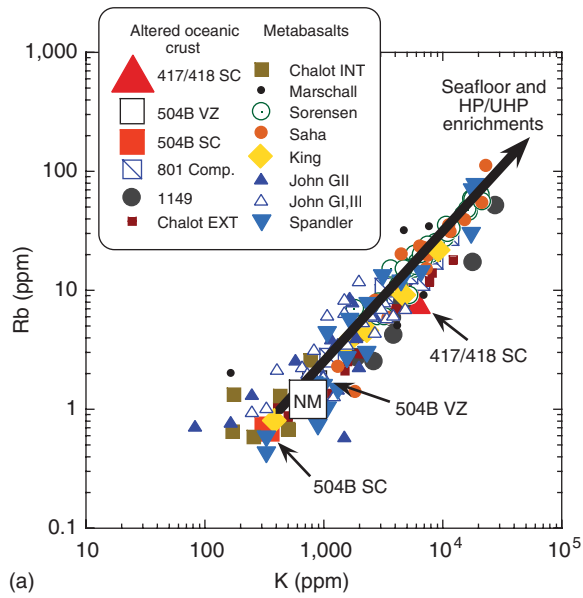
In summary, the potassium, barium, rubidium, thorium, uranium, lead, and cerium inventories in subducting altered oceanic crust appear to be largely retained to depths of at least 90–100 km, with some potassium, barium, rubidium, lead, and thorium enrichment occurring during subduction-zone metamorphism (see [Spandler *et al.*, 2004](#); [John *et al.*, 2004](#); [Figures 7, 8b, and 8d](#)). These elements could thus, at greater depths, be available in the generation of arc lavas and perhaps partly subducted into the mantle beyond subarc depths. There is some indication that uranium, barium, potassium, and LREE are lost from some rocks during dehydration in the deep forearc, perhaps particularly in zones of higher fluid flux (see [Figures 7b, 8a, and 8d](#); cf. [Becker *et al.*, 2000](#); [Spandler *et al.*, 2004](#); [John *et al.*, 2004](#)). Small degrees of loss (e.g., those proposed by [Zack *et al.*, 2001](#)) could be obscured by the large compositional ranges that are observed in the protoliths. The relationships in [Figures 7 and 8](#) highlight the need to assess degrees of element

mobility through careful field sampling and petrologic study, such as in the recent study of [John *et al.* \(2004\)](#), who demonstrated fractionation of certain trace elements in vein envelopes representing zones of higher fluid flux.

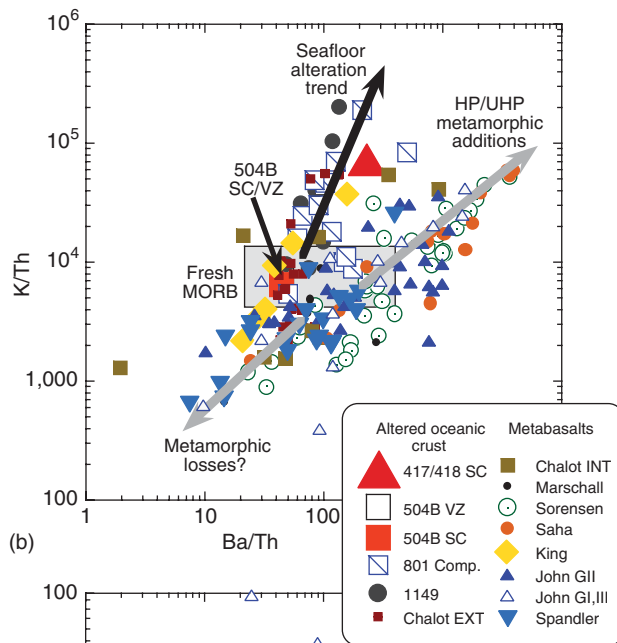
3.20.5.3.2 Summary and remaining important issues

This section highlights several of the more significant conclusions reached through geochemical study of subduction-zone chemical cycling based on certain HP and UHP eclogites, and includes brief discussion of a couple of the most limiting remaining uncertainties in reconstructing the chemical effects of prograde subduction on oceanic crust based on study of such rocks. Perhaps the, when the range of possible protoliths is fully considered important conclusion to be drawn from study of subduction-zone eclogites is that, when the range of possible protoliths is fully considered, most show little evidence for loss of trace elements for which slab additions to arc source regions are invoked (e.g., boron, lithium, cesium, barium, uranium, and thorium; see [Chalot-Prat *et al.*, 2003](#); [Spandler *et al.*, 2004](#); [Philipot and Selverstone, 1991](#); [John *et al.*, 2004](#); [Marschall *et al.*, 2006](#)). Similarly, such rocks commonly show little or no stable isotope or fluid inclusion evidence for open-system behavior ([Nadeau *et al.*, 1993](#); [Barnicoat and Cartwright, 1995](#); [Cartwright and Barnicoat, 1999](#)) and instead show the preservation of isotopic signatures obtained on the seafloor. [John *et al.* \(2004\)](#) suggested some localized element mobility, perhaps related to high-fluid flux zones, which resulted in fractionation of light rare earth element (LREE) from heavy rare earth element (HREE) and high-field

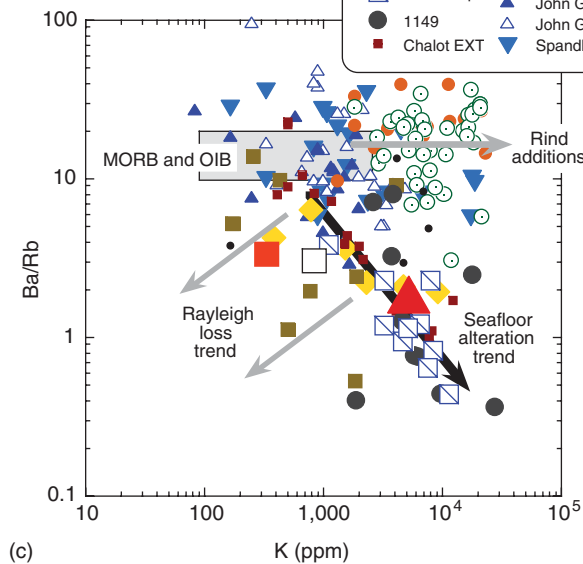
Figure 7 Relationships among the LILE and Th in HP and UHP metamorphosed basalt and gabbro, compared to altered oceanic basalts. This figure illustrates the difficulties in deconvoluting seafloor and subduction-zone metamorphism effects (e.g., for K and Rb data; see (a)), and the possible use of Ba–K enrichments to distinguish between these two histories ((b) and (c)). The data plotted in these figures are from [Spandler *et al.* \(2004; for New Caledonia\)](#), [John *et al.* \(2004; for Zambia; data broken into groups, Group II and Groups I and III\)](#); [King *et al.* \(2004\)](#) and [King \(2006; for Lago di Cignana\)](#), [Sorensen *et al.* \(1997; tectonic blocks\)](#), [Saha *et al.* \(2005; tectonic blocks\)](#), [Marschall *et al.* \(2006; Syros\)](#), [Chalot-Prat *et al.* \(2003; Alps internal units\)](#), [Chalot-Prat \(2005, external units\)](#), [Staudigel *et al.* \(1996; ODP Sites 417 and 418 supercomposite\)](#), [Peucker-Ehrenbrink *et al.* \(2003; ODP Site 504B supercomposite and composite for volcanic zone\)](#), and [Kelley *et al.* \(2003; ODP Sites 801 and 1149\)](#). NM, N-MORB (from [Hofmann, 1988](#)). In (b) and (c), note the distinct trends for samples of seafloor altered basalt (“Seafloor alteration trend”) and for HP and UHP additions (“Rind additions” and “HP/UHP metamorphic additions”). Note that this figure and [Figure 8](#) do not for the most part distinguish between textural varieties and structural settings for these samples, and are intended to show gross trends only for seafloor alteration and HP/UHP metamorphic processes. On these plots, the rinds, some of which have undergone significant amounts of deformation and volume strain (see [Sorensen and Grossman, 1989](#); [Sorensen *et al.*, 1997](#); [Bebout and Barton, 2002](#)), are regarded as endmember cases of fluid–rock interaction (i.e., rocks known to have experienced metasomatic alteration during HP metamorphism). On (c), the trend for Rayleigh loss (labeled arrows pointing to the lower left) was calculated by [Zack *et al.* \(2001\)](#).



(a)



(b)



(c)

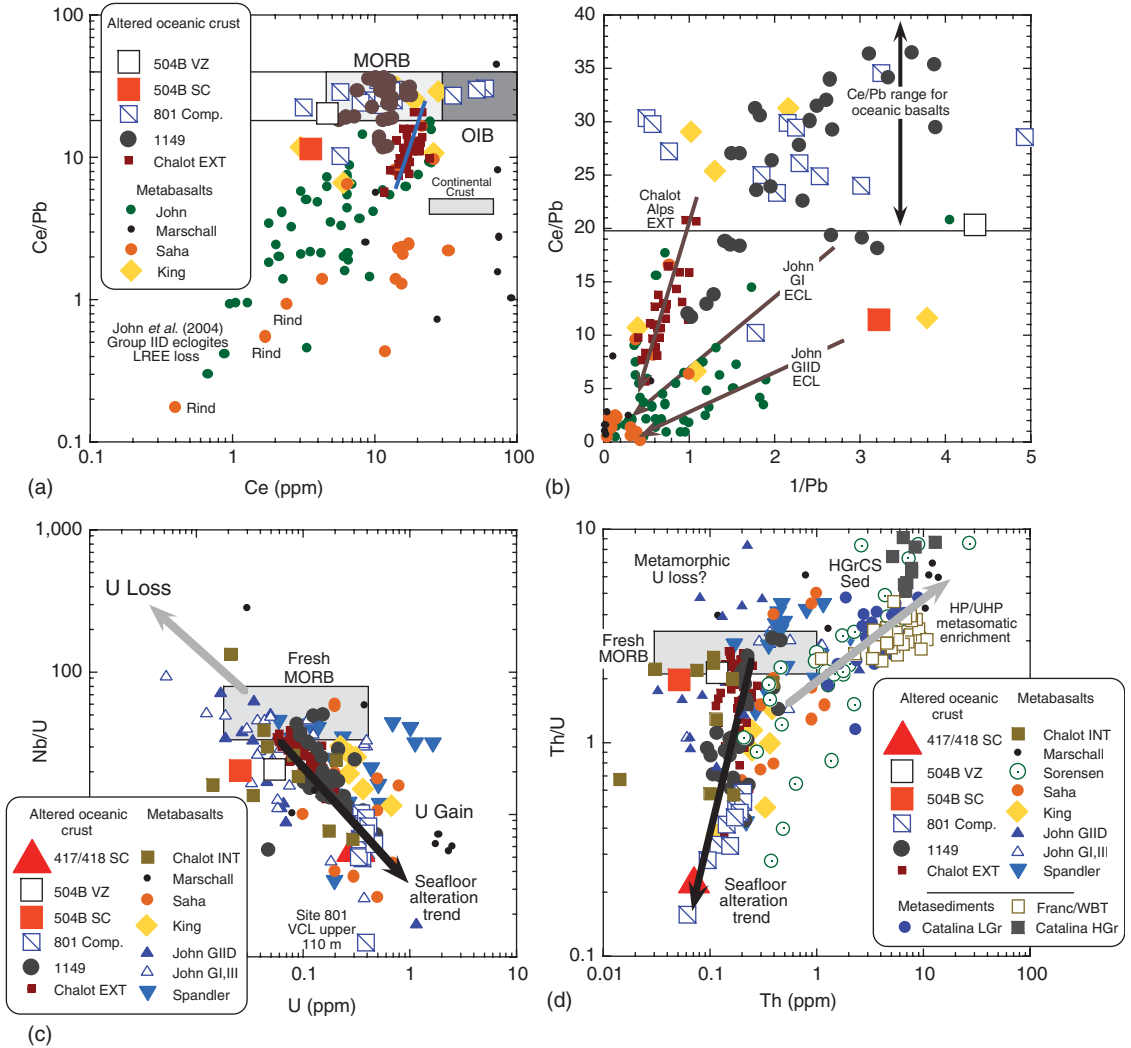


Figure 8 Relationships among Th, U, Pb, Ce, and Nb in HP and UHP metamorphosed basalt and gabbro, compared to altered seafloor basalts. Varying overlap in the two data sets produces difficulties in deconvoluting seafloor and subduction-zone metamorphism effects. In (a) samples with low Ce concentrations and correspondingly lower Ce/Pb are either metasomatic rinds on tectonic blocks (data from [Saha et al., 2005](#)) or more extensively metasomatized Group II eclogites of [John et al. \(2004\)](#). In (b), many of the HP and UHP rocks show enrichments in Pb (some also with decreased Ce concentrations; see (a)) and resulting lowered Ce/Pb, and the data for some eclogites (Groups I and IID of [John et al., 2004](#); “John GI ECL” and “John GIID ECL”) produce enrichment trends toward higher Pb concentrations and lower Ce/Pb, as do the very low-grade metabasalts from the Alps external units investigated by [Chalot-Prat et al. \(2003\)](#); “Chalot Alps EXT”; ophiolitic and not directly representative of seafloor basalts; trend indicated by light blue line). Note the nearly complete overlap in Nb–U data for the seafloor altered basalts and HP and UHP metamorphosed equivalents (c). In the plot of Th concentrations versus Th/U in (d), seafloor altered basalts show a distinct trend toward lower Th resulting from U enrichment relative to Th, whereas metasomatic rinds (some of the data from “Sorensen” and “Saha”) are enriched in Th relative to seafloor altered basalts. Also shown in (d) are Th–U data for low- and high-grade metasedimentary rocks of the Catalina Schist (data from [Bebout et al., 1999](#)). High-grade Catalina Schist metasedimentary rocks have higher Th/U than lower-grade equivalents, likely related to U loss with or without some Th enrichment during partial melting. The data plotted in these figures are from [Spandler et al. \(2004\)](#); for New Caledonia), [John et al. \(2004\)](#); for Zambia); data broken into groups, Group II and Groups I and III); [King et al. \(2004\)](#) and [King \(2006\)](#); for Lago di Cignana), [Sorensen et al. \(1997\)](#); tectonic blocks and rinds), [Saha et al. \(2005\)](#), tectonic blocks and rinds), [Marschall et al. \(2006\)](#); for Syros), [Bebout et al. \(1999\)](#); Catalina Schist metasedimentary rocks, broken into low-grade (LGr) and high-grade (HGr)), [Sadofsky and Bebout \(2003\)](#); for Franciscan Complex and Western Baja Terrane, metasedimentary rocks), [Chalot-Prat et al. \(2003\)](#); for Alps internal units), [Chalot-Prat \(2005\)](#); for Alps external units), [Staudigel et al. \(1996\)](#); ODP Sites 417 and 418 supercomposite), [Peucker-Ehrenbrink et al. \(2003\)](#); ODP Site 504B supercomposite and composite for volcanic zone), and [Kelley et al. \(2003\)](#); ODP Sites 801 and 1149). NM, N-MORB (from [Hofmann, 1988](#)). In (d) note the distinct trends for samples of seafloor altered basalt (“Sea floor alteration trend”) and for HP and UHP additions (“HP/UHP metamorphic additions”).

strength element (HFSE) in some eclogites. Moreover, for lower-*P* paleoaccretionary systems (e.g., Catalina Schist), fluid and element mobility is heterogeneous, and enhanced in zones of higher permeability related to deformation (see [Bebout, 1991b, 1997](#)), with the more coherent nonmélange zones appearing to have behaved as closed systems.

Many HP and UHP eclogites in fact show enrichments in the elements thought to be removed from subducting oceanic crust beneath arcs. Some mafic blocks contained in metasedimentary or metaultramafic mélange experienced hydration and alteration of some of their major and trace-element and isotope signatures due to transfer from the surrounding sedimentary and ultramafic lithologies ([Bebout and Barton, 1989, 1993](#); [Bebout, 1997](#); [Sorensen and Grossman, 1989, 1993](#); [Nelson, 1995](#); [Sorensen et al., 1997](#); [Zack et al., 2001](#); [Saha et al., 2005](#)). The element enrichments in metasomatic rinds, and veins and their metasomatic envelopes, serve as excellent records of the relative mobility of major and trace elements in the HP and UHP fluids.

When loss-on-ignition (LOI) data (presumably representing H₂O contents) are compared for blueschist- and eclogite-facies rocks, as expected, eclogite-facies rocks do generally have lower H₂O contents consistent with significant H₂O loss over the blueschist–eclogite transition. Perhaps more interesting than this systematic difference, explained simply by the less hydrous mineral assemblages, is the question of whether or not HP mafic rocks are hydrated during early stages of metamorphism i.e., whether their H₂O contents are, at least at shallow levels of subduction zones, higher than those of their seafloor protoliths. As with the comparisons of major and trace-element, and isotope compositions, the problem in testing this hypothesis relates to the large variability in composition of the presumed seafloor protolith sections (see [Staudigel et al., 1996](#); Chapter 3.15).

These several conclusions point to what is certainly one of the key remaining questions pertaining to the use of the geochemistry of HP and UHP eclogites to reconstruct deep subduction-zone chemical evolution, that is, the extent to which the compositions of these eclogites are indeed representative of processes operating “normally” along the slab–mantle interface. Whereas a number of the ophiolitic sequences in the Italian and French Alps (and elsewhere) are relatively coherent and obviously representative of seafloor basalt, mafic blocks in mélanges do not obviously represent samples of the intact subducted slab and may show enhanced metasomatism due to their

occurrence in zones of high fluid flux. Uncertainty remains regarding the volumetric significance of mélange-like zones at depth in modern subduction zones.

[Yamamoto et al. \(2002\)](#) compared the major and trace-element compositions of UHP Kockchetav Massif metabasites, ranging in grade from amphibolite and quartz–amphibole eclogite, to coesite–zoisite eclogite and diamond eclogite (*P–T* for the latter two groups of samples are 2.8–3.1 GPa, 660–740 °C, 6.0 GPa, 950 °C), and found loss of LILE with increasing metamorphic grade. A more thorough examination of these and other eclogites representing such extreme metamorphic conditions is warranted. As noted above (see [Figure 6](#)), a number of UHP suites record peak *P–T* conditions that straddle or are above the H₂O-saturated solidi, and could provide insight into the chemical effects of melt release that may occur beneath some modern arcs (see the thermal models in [Figure 3](#); data presented by [Becker et al., 2000](#) for rocks with peak *P–T* above the wet solidi).

3.20.5.4 Geochemical Studies of HP and UHP Metasedimentary Rocks

HP and UHP metasedimentary rocks are the subject of fewer geochemical studies than corresponding mafic rocks, as most occur in paleoaccretionary complexes, representing relatively shallow levels of accretionary systems. Moreover, metasedimentary suites derived from deeper regions of subduction zones show more extensive retrograde overprints related to exhumation than mafic rocks in the same suite (see [Proyer, 2003](#); [Fitzherbert et al., 2005](#)), thus complicating efforts to identify changes due to prograde, subduction-zone metamorphism.

The Catalina Schist, and similar forearc metasedimentary rocks in the Franciscan Complex and Western Baja Terrane, have been extensively studied in order to define the degree of devolatilization and related chemical change that occur during subduction to depths of ~40 km. With the exception of the higher-grade units in the Catalina Schist (epidote-amphibolite and amphibolite facies), these rocks experienced subduction along a range of relatively cool *P–T* paths like those experienced in thermally mature modern subduction zones ([Sadofsky and Bebout, 2003](#); [Figure 9](#)). Metasedimentary rocks in these suites are compositionally similar to the terrigenous component in GLOSS ([Figure 10](#)), which constitutes ~76 wt.% of this composite ([Plank and Langmuir, 1998](#)). Although these HP

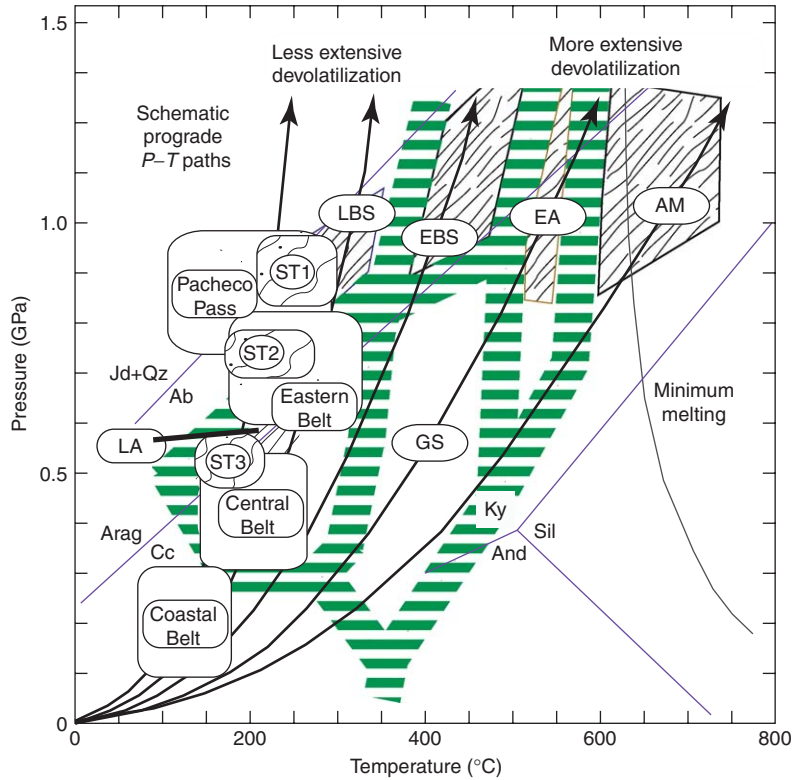


Figure 9 *P-T* diagram showing the peak metamorphic conditions and prograde paths of the units of the Catalina Schist (from Grove and Bebout, 1995; see sources of metamorphic facies stability fields and some key reactions therein). Also shown are the estimates of peak metamorphic conditions of the units of the Coast and Diablo Ranges Franciscan Complex, California, and the Western Baja Terrane (Mexico; see Sadofsky and Bebout (2003) for sources of *P-T* data). Note that the higher-grade units of the Catalina Schist (epidote-amphibolite (EA) and amphibolite (AM)) were peak-metamorphosed at anomalously high temperatures relative to those in most modern subduction zones (see review of recent thermal models by Peacock, 2003), whereas the low-grade units of the Catalina Schist (lawsonite-albite (LA), lawsonite-blueschist (LBS), and even epidote-blueschist (EBS)), and the various units of the Franciscan Complex in the Coast and Diablo Ranges, California (“Coastal Belt,” Central Belt,” “Eastern Belt,” and “Pacheco Pass”), and in the Western Baja Terrane (Baja, Mexico; “ST1,” “ST2,” and “ST3”), are more compatible in their peak *P-T* with conditions in modern margins.

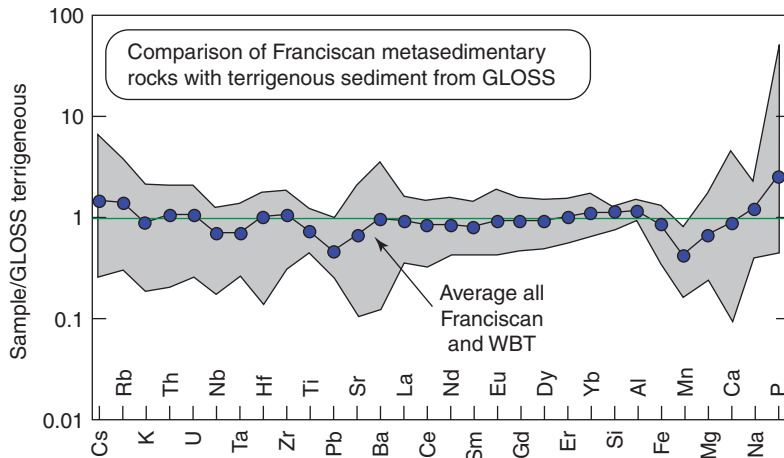


Figure 10 Plot of trace elements, in order of increasing compatibility during partial melting in the mantle (to the right; normalized to the GLOSS composite of Plank and Langmuir, 1998), for metasedimentary rocks of the Franciscan Complex and Western Baja Terrane (from Sadofsky and Bebout, 2003). The data are normalized to the mean composition of “terrigenous sediment” within GLOSS.

metasediments have much lower LOI (mostly representing H₂O contents; see Figure 4) than those of seafloor sediments, they retain much of their original inventories of even relatively fluid-mobile elements (cesium, boron, arsenic, and antimony) except in tectonometamorphic units in the Catalina Schist representing prograde metamorphism along prograde *P–T* paths warmer than those experienced in most modern subduction zones (Figure 11, Sadofsky and Bebout, 2003).

The protoliths of the Schistes Lustres, exposed in NW Italy, are believed to represent deep-sea sediment somewhat similar to the section at ODP Site 765, containing a significant carbonate component (Banda forearc; see Deville *et al.*, 1992; Agard *et al.*, 2002; and references therein). Together with the UHP metasedimentary rocks at Lago di Cignana (Reinecke, 1998), they have been studied to reconstruct their devolatilization histories to depths of ~90 km in relatively cool subduction zones (see Busigny *et al.*, 2003; Bebout *et al.*, 2004). Busigny *et al.* (2003), who measured their LILE concentrations, nitrogen concentrations, and isotope compositions, determined that the Schistes Lustres, and even the Lago di Cignana rocks (representing somewhat greater depths at higher temperatures) resemble their presumed sedimentary protoliths. These authors concluded that, in the relatively cool subduction zone that produced these rocks, the original element concentrations and the nitrogen-isotope compositions were preserved to depths of ~90 km. Mahlen *et al.* (2005) concluded that prograde metamorphism did not noticeably change the rare earth element (REE) concentrations or disrupt the Rb–Sr systematics in similar rocks. One important issue, however, in the work on this suite, and most other UHP metamorphic suites, concerns the effects of exhumation history on the prograde records of devolatilization (see Bebout *et al.*, 2004 and discussion of exhumation history by Agard *et al.*, 2002, in which argon data indicate some neoblastic mica growth during retrogression). For the traverse of the Schistes Lustres studied by Busigny *et al.* (2003), and in Lago di Cignana metasedimentary rocks, ion microprobe (secondary ion mass spectrometry (SIMS)) analyses of micas showing textures and mineral chemistry consistent with prograde growth show only subtle trends in relatively fluid-sensitive element concentrations and ratios (e.g., B/Li) as a function of increasing metamorphic grade (Figure 12, from Bebout *et al.*, 2004), an observation crudely consistent with the conclusions of Busigny *et al.* (2003). For the Cignana metasedimentary rocks, Reinecke (1998) concluded that little or no record is

preserved of the prograde history, and that what exists is in the form of mineral inclusions and mineral chemistry in a small number of particularly “robust” phases (garnet, tourmaline, zircon, apatite, and dolomite). The lack of an obvious modification in whole-rock trace-element concentrations, despite significant overprinting during exhumation, would imply that the rocks behaved largely as closed systems during this later history, experiencing only redistribution of trace elements among the minerals in the evolving mineral assemblages. Boron-isotope analyses of Cignana metasedimentary tourmalines containing coesite inclusions identified zones near tourmaline rims that are clearly exhumation-related and possibly represent open-system behavior (Bebout and Nakamura, 2003).

The similarity in Cs/Rb of seafloor sediment, including Sites 765 and 1149 (sampling seafloor sediments over the full range of terrigenous, pelagic, and carbonate compositions), the Schistes Lustres, and the lower-grade metasedimentary rocks of the Catalina Schist and other circum-Pacific paleoaccretionary suites, suggests that the Rb–Cs signature of seafloor sediments remains largely intact to depths of up to ~90 km in relatively cool subduction zones (see Figure 13). Higher-grade metasedimentary rocks from the Catalina Schist (labeled, “LBS,” “EBS,” “EA,” and “AM” in Figure 13) have lower Cs/Rb and experienced more extensive devolatilization along warmer prograde *P–T* paths (see Figures 9 and 11; discussion of the tectonometamorphic history of these units by Grove and Bebout, 1995).

Deeply subducted metasediments also afford an analysis of the cycling of organic carbon (and nitrogen) into the mantle, and some considerable attention has been paid to this “organic connection” (see Bebout and Fogel, 1992; Bebout, 1995; Sadofsky and Bebout, 2003; Busigny *et al.*, 2003). As discussed above in sections dealing with diagenesis, early-stage heating of organic matter in forearcs leads to the production of relatively devolatilized, amorphous carbonaceous matter that largely retains the organic/reduced carbon-isotope signatures of the seafloor sediment. Progressive recrystallization toward graphite occurs with heating and time, as documented by Beyssac *et al.* (2002), and this graphitization promotes carbon-isotope exchange with other organic-reduced carbon reservoirs in the same rocks, primarily carbonate. Interestingly, nitrogen initially bound in clays and organic matter in sediments is redistributed rather efficiently into low-grade white micas (see Bebout, 1995), and whole-rock C/N ratios of seafloor sediment appear to be retained, despite this mineralogical

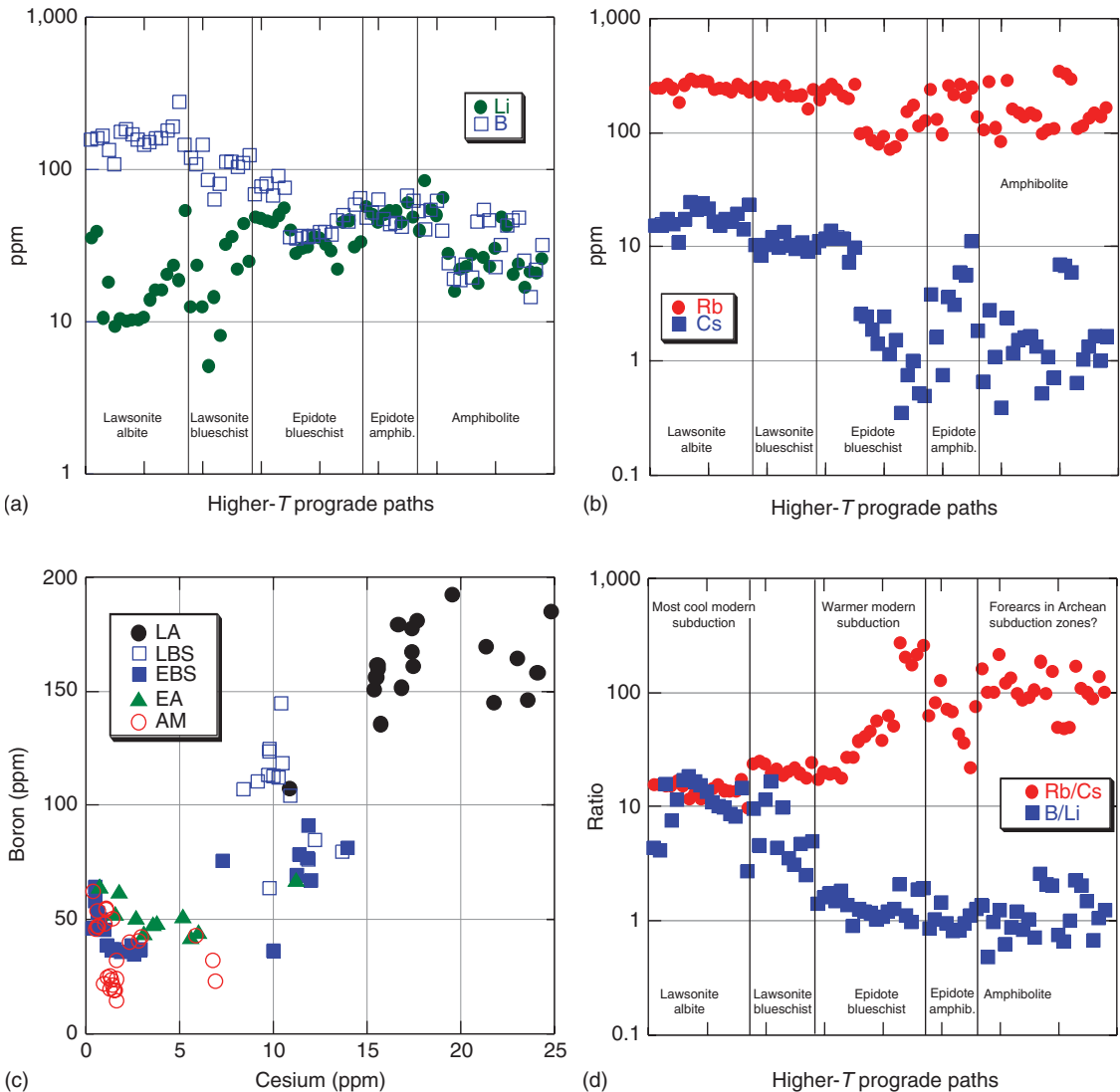


Figure 11 Plots illustrating variable concentrations of B, Li, Cs, and Rb in white micas in Catalina Schist metasedimentary rocks with increasing metamorphic grade (to the right in (a), (b), and (d)). (a) Plot of B and Li white-mica concentrations versus grade, demonstrating decreasing white-mica B concentrations, and increasing white-mica Li concentrations, in rocks experiencing paths into metamorphic grades of epidote-blueschist and higher. (b) Plot of Rb and Cs white-mica concentrations versus grade, demonstrating relatively uniform Rb concentrations across grades, and decreasing Cs concentrations in white micas in rocks experiencing paths into metamorphic grades of epidote-blueschist and higher. (c) Plot of Cs versus B in white micas in the Catalina Schist metasedimentary rocks, demonstrating correlated decreases in concentration in higher-grade units. LA, lawsonite-albite; LBS, lawsonite–blueschist amphibolite; EA, epidote-amphibolite; EBS, epidote-blueschist (d) Changes in Rb/Cs and B/Li with increasing metamorphic grade. The metamorphic temperatures, for these depths (see Figure 9), are compatible with those expected for modern cooler and warmer subduction, and the high temperatures represented by the epidote-amphibolite and amphibolite units could be similar to those experienced in Archean subduction zones. These data thus indicate efficient retention of B and Cs to 40 km depths in cooler modern subduction zones, but significant B and Cs loss in the warmer modern margins and in Archean subduction zones. In these rocks, B, Cs, and Rb are nearly entirely sited in the white micas, whereas Li residency is more complex, with significant concentrations also in chlorite in the lower-grade units (see [Bebout *et al.*, 1999](#), in press).

separation of the carbon and nitrogen organic components. [Sadofsky and Bebout \(2003\)](#) (also see [Bebout, 1995](#)) found little modification of the organic C–N signature in metasedimentary rocks subducted to depths of up to ~40 km

in a paleoaccretionary prism. As discussed in later sections, any disruption of the organic C–N reservoir conveyed into subduction zones could affect convergent margin C–N mass balance and potentially the carbon- and

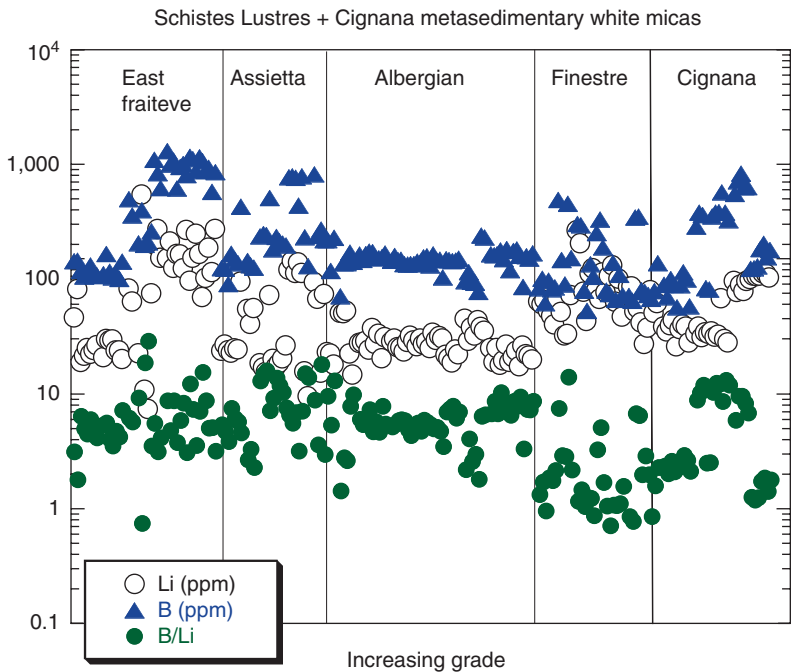


Figure 12 Concentrations of B and Li, and B/Li ratios, in phengite (data for paragonite excluded, where present in these samples, as much of it appears late-stage and exhumation-related based on textures) as a function of increasing metamorphic grade (to the right) in exposures of the Schistes Lustres in the Cottian Alps (see [Agard et al., 2002](#)). Not included in this plot are data for phengite occurring as inclusions in garnet in rocks from Lago di Cignana; these phengites have higher B and related higher B/Li. Data from [Bebout et al. \(2004\)](#).

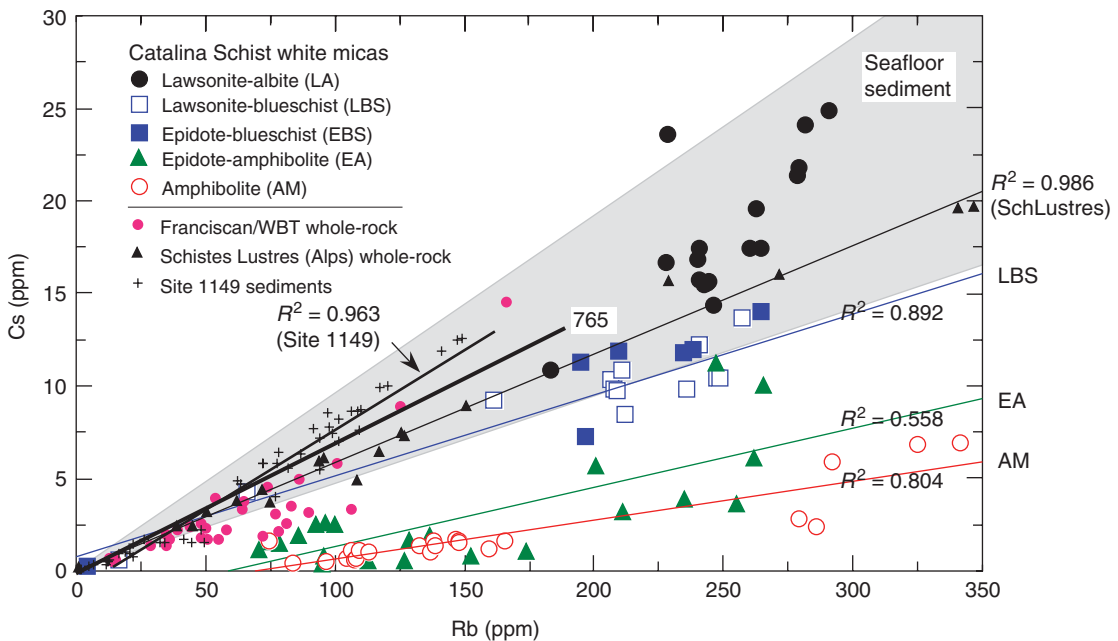


Figure 13 Comparison of Catalina Schist Rb–Cs white-mica compositions with the range of Rb/Cs of seafloor sediments (shaded region), the latter from [Ben Othman et al. \(1989\)](#) and [Plank and Langmuir \(1998\)](#) with data for seafloor sediment from ODP Site 765 (Banda forearc), from [Plank and Ludden \(1992\)](#) and data for ODP Site 1149 (Izu-Bonin) from T. Plank and K. Kelley (personal communication). Also shown, for comparison, are data for Franciscan and Western Baja Terrane (“WBT”) metasedimentary rocks (from [Sadofsky and Bebout, 2003](#)) and for the Schistes Lustres (from [Busigny et al., 2003](#)).

nitrogen-isotope budgets in the deep mantle (see discussions in [Sadofsky and Bebout, 2003](#); [Li and Bebout, 2005](#); [Bebout and Kump, 2005](#)).

3.20.5.5 HP and UHP Ultramafic Rocks and Mélange

There has been growing interest in the compositions of hydrated ultramafic rocks and the degree to which these compositions can be used to infer slab fluxes of trace elements at greater depths in subduction zones, including arc source regions (see [Hattori and Guillot, 2003](#); [Tenthorey and Hermann, 2004](#); [Scambelluri et al., 2004a, b](#); [Chalot-Prat et al., 2003](#)). [Straub and Layne \(2003\)](#) suggested that “wedge serpentinite” dragged beneath the Izu volcanic front is the source of a number of trace elements (fluorine, chlorine, H₂O, lithium, and isotopically heavy boron) via dehydration and release to the subarc mantle (also see [Hattori and Guillot, 2003](#); [Scambelluri et al., 2004b](#)). Deeply subducted, variably serpentinized oceanic lithospheric mantle has increasingly been called upon to produce large amounts of H₂O that could convey slab and sediment chemical signatures into arc source regions (e.g., [Rupke et al., 2002, 2004](#); [Ranero et al., 2005](#); see [Sharp and Barnes, 2004](#) for discussion of possible Cl subduction in seafloor serpentinites; [Fruh-Green et al., 2001](#) for discussion of O–H isotope compositions of HP ultramafic rocks in the Western Alps).

Mélange formation processes involving coeval metasomatic and mechanical mixing, are yet another means by which rocks can be “hybridized” at depth in subduction zones (see [Bebout and Barton, 1989, 1993, 2002](#); [Breeding et al., 2004](#); [King et al., 2006](#)). [Figures 14 and 15](#) present whole-rock trace-element data for hybrid mélange rocks from the Catalina Schist (lawsonite–albite, lawsonite–blueschist, and amphibolite facies), demonstrating the extremely wide range of rock compositions that can result from this process. These mélange rocks bear little resemblance to any of their sedimentary, mafic, and ultramafic protolith mixing compositions, and any fluids interacting with them could have inherited chemical compositions reflecting hybridized sources (see discussion by [King et al., 2006](#)). The production of such lithologies at the slab–mantle interface could not only strongly impact the geochemical evolution in this region, but also stabilize large amounts of volatiles to great depths in high-variance assemblages containing minerals such as chlorite, talc, and

amphibole ([Bebout and Barton, 2002](#)). Relative to a simple (mechanical) mixture of known mélange-mixing components (mafic, ultramafic, and sedimentary), some of these rocks are depleted in certain trace elements (e.g., cesium, rubidium, and barium), suggesting the removal of these elements in metasomatizing fluids (see [Bebout and Barton, 2002](#); [King et al., 2006](#)).

3.20.5.6 Metasomatic Rinds on Blocks in Tectonic Mélange

Metasomatic rinds on mafic, ultramafic, and sedimentary blocks floating in HP mélange of varying compositions allow one to characterize metasomatism that can be directly related to subduction-zone processes (see [Sorensen and Grossman, 1989, 1993](#); [Sorensen et al., 1997](#); [Bebout and Barton, 1993, 2002](#); [Breeding et al., 2004](#); [Saha et al., 2005](#); see data in [Figures 7 and 8](#)). [Bebout and Barton \(2002\)](#) demonstrated that the matrix in the high-grade mélange in the Catalina Schist was in part produced by incorporation of rinds developed on these three lithologies ([Figure 14](#)), thus, that rind formation represents initial stages of the mixing leading to mélange matrix formation. [Breeding et al. \(2004\)](#) demonstrated that metasomatic exchange between sedimentary rock and adjacent ultramafic mélange matrix resulted in dramatic depletions, in the altered sedimentary rock, in many trace elements of interest in studies of arc lavas ([Figure 16](#)). These depletions were related to the destabilization of key host phases such as mica and by interaction of the metasedimentary phases with mélange-equilibrated fluids that were strongly depleted in elements such as the LILE, uranium, and lead.

3.20.5.7 Records of Fluid/Element Mobility in Veins, Isotopic Compositions, and Fluid Inclusions

Metamorphic veins provide an additional, albeit complex, record of fluid and element mobility during various stages of metamorphism of HP and UHP rocks. Veins leave behind high-variance mineral assemblages that are, in general, regarded as fractionated residues of the fluids that produced them (see [Bebout and Barton, 1993](#); [Becker et al., 1999](#)). However, vein mineralogy, trace element, and stable isotope compositions can be used to estimate fluid compositions (given the availability of constraints on the conditions of their formation), and combined with their

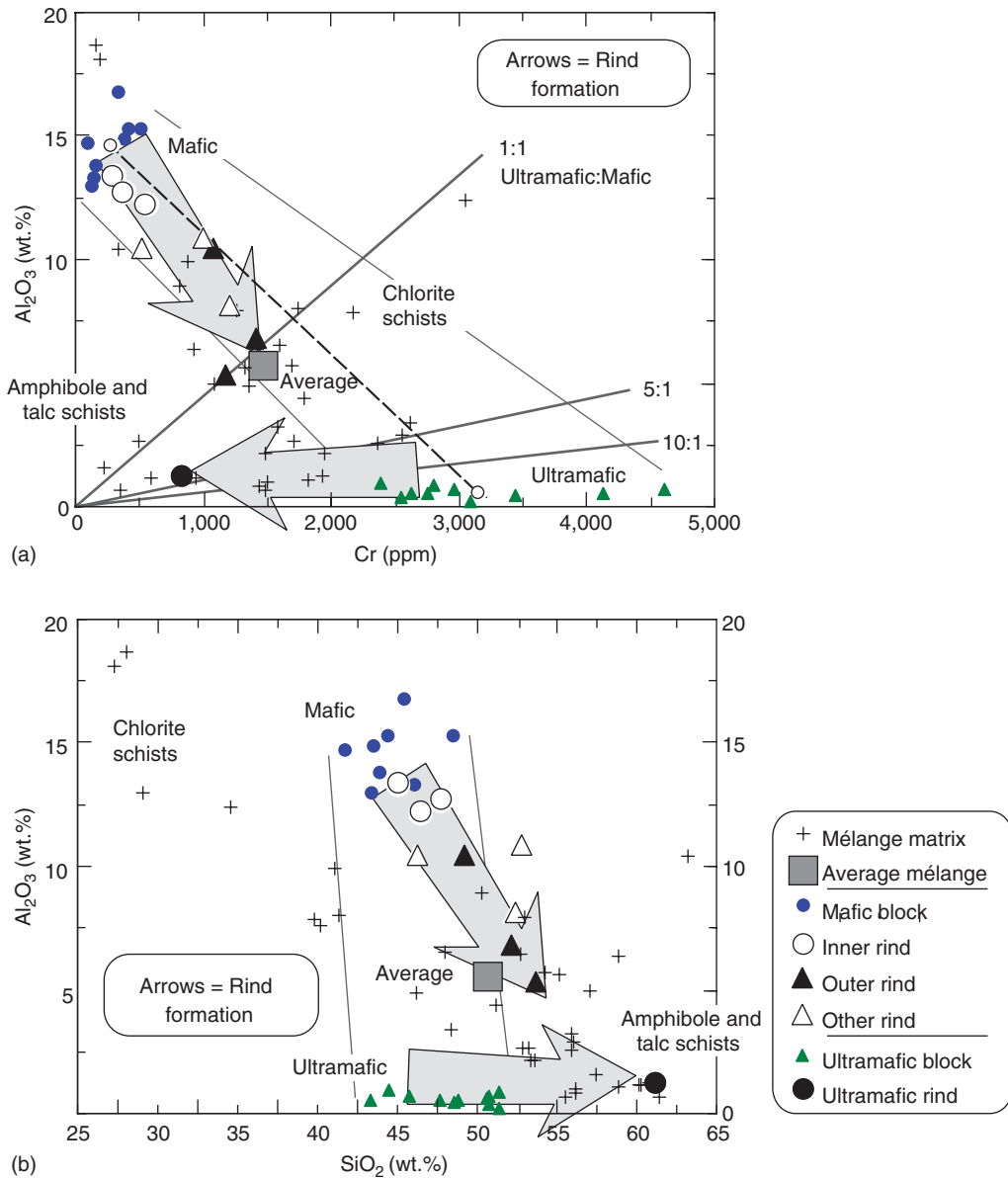


Figure 14 Cr–Al–Si compositions for mélangé matrix and likely mélangé mixing components in the amphibolite unit of the Catalina Schist. In both (a) and (b), the large arrows indicate the trends from tectonic block compositions observed in metasomatic rinds on the mafic and ultramafic blocks. Reproduced with permission from [Bebout and Barton \(2002\)](#).

Sr–Nd–Pb–Os-isotope compositions, can be used to trace fluid sources. There has been great interest in whether or not vein networks in HP and UHP eclogites and metasedimentary rocks reflect large-scale fluid transport or local-scale segregations. Two common observations are that (1) trace elements enriched in veins are not obviously depleted in nearby host-rocks, and that the veins are in trace-element (and isotopic) equilibrium with host-rocks, and (2) some detailed studies of vein–vein haloes–host rocks clearly indicate relatively local-scale diffusion of trace elements into veins ([Philippot](#)

and [Selverstone, 1991](#); [Widmer and Thompson, 2001](#)). These observations suggest that elements primarily diffused into the fractures on a local scale, rather than being introduced from external sources. However, they do not preclude movement of fluids along the fractures (after all, once in the fractures, the fluid is gone from the system). Both [Molina *et al.* \(2004\)](#) and [Brunsmann *et al.* \(2000, 2001\)](#) argued for local-scale element transport of unknown scale. Interestingly, vein mineralogy commonly includes phases rich in elements thought to be relatively immobile (titanium, aluminum, and

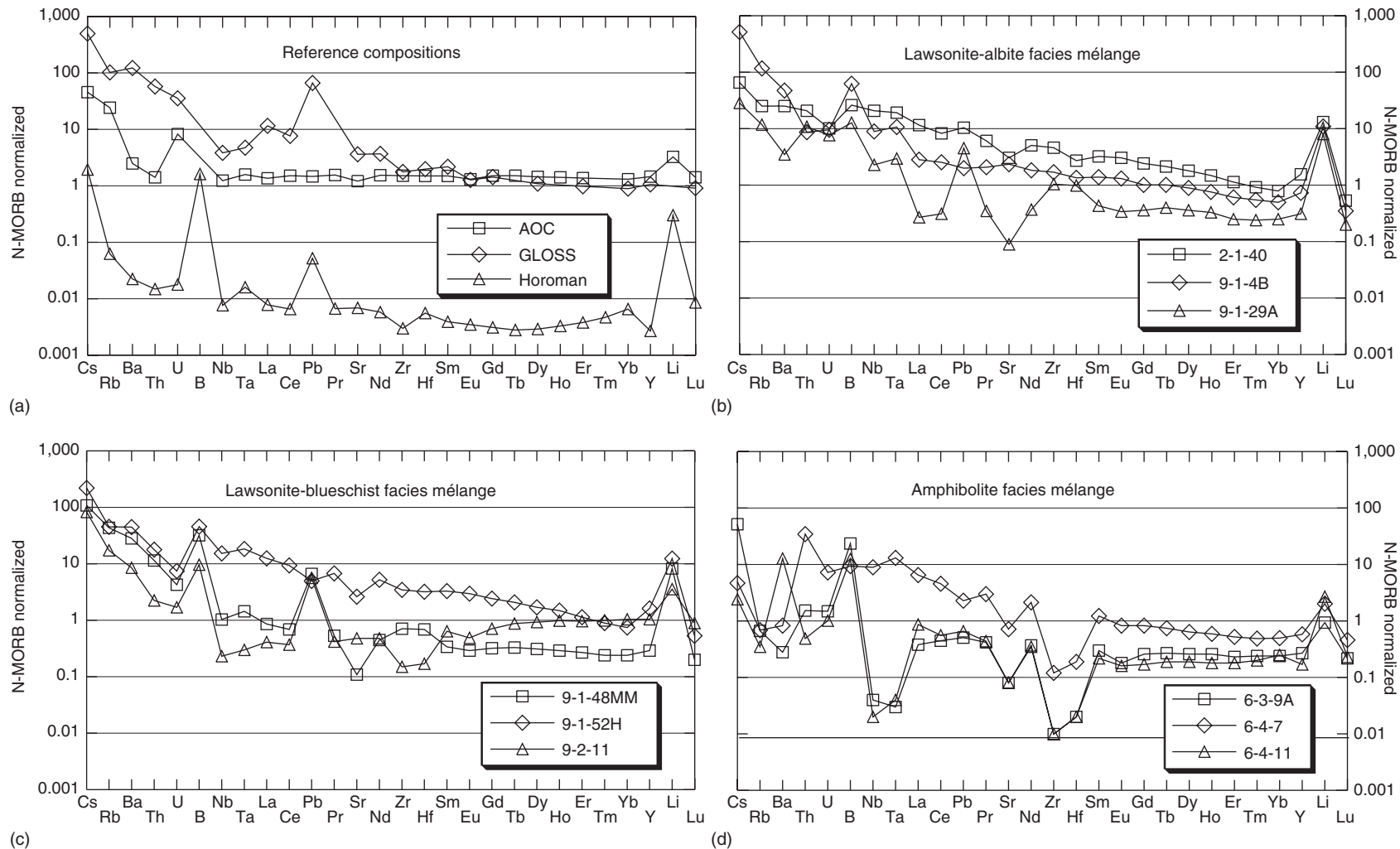


Figure 15 Concentrations of trace elements in Catalina Schist mélanges matrix (lawsonite-albite (b), lawsonite-blueschist (c), and amphibolite (d) grades) (see [Grove and Bebout, 1995](#) for discussion of tectonometamorphic evolution), relative to the N-MORB composition of [Hofmann \(1988\)](#), the GLOSS sediment composite from [Plank and Langmuir \(1998\)](#), the altered oceanic crust composite for Site 417 from [Staudigel et al. \(1996\)](#), and data for the Horoman peridotite from [Tanimoto \(2003\)](#), with elements in order of increasing compatibility during mantle melting to the right (from [King et al., 2006; King, 2006](#)). Note that the compositions of the mélanges matrix samples bear little resemblance to compositions for the presumed mixing components involved in their production (see compositions of altered oceanic crust, seafloor sediment, and peridotite in (a)).

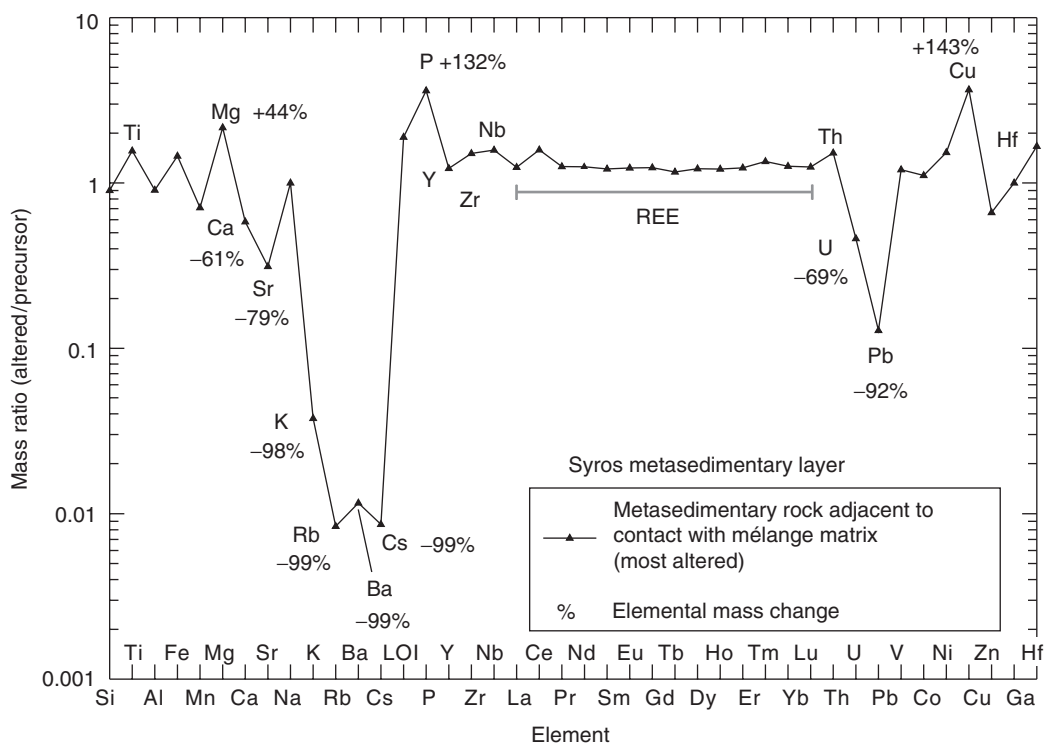


Figure 16 Plot of trace-element concentrations in metasedimentary rock having undergone metasomatic exchange with ultramafic mélangé matrix, relative to the concentrations in the same layer but away from the interface with this mélangé matrix (the “precursor”). Reproduced by permission of Geological Society of America from [Breeding *et al.* \(2004\)](#).

zirconium), demonstrating at least local-scale diffusive transfer of these elements, likely via an intergranular fluid.

[Spandler and Hermann \(2006\)](#) review the utility of vein mineralogy and major and trace-element compositions for evaluating mobility in and from subducting oceanic crust. They suggest that fluids released during the blueschist-to-eclogite transition at 50–80 km could be trapped in impermeable eclogitic rocks and dragged beneath arcs to contribute to their source regions. [Widmer and Thompson \(2001\)](#) discussed the expectations for local versus open-system redistribution and concluded that the veins they investigated (in the Zermatt-Saas Zone, Switzerland) are local-scale segregation phenomena, not channel ways for larger-scale fluid transport (also see the stable isotope study of Alpine veins by [Cartwright and Barnicoat, 1999](#)). [John and Schenk \(2003\)](#) argued that the blueschist-eclogite and gabbro-eclogite transitions are kinetically controlled, and that channelized infiltrating fluids, producing veins with large grains of omphacite, kyanite, and garnet, enhanced these transitions in rocks from Zambia (also see evidence for LREE fractionation in these infiltrated rocks in [John *et al.*, 2004](#)). [John *et al.* \(2004\)](#) suggested that the fluids were produced by dehydration in underlying

hydrated mantle rocks in the subducting slab. Because fluid pathways are zones where mineral replacements are the most kinetically favored (see [John *et al.*, 2004](#)), veins and their haloes in host-rocks can provide the best records of exhumation history (also see [van der Klaww *et al.*, 1997](#)).

Isotopes can, in some cases, provide a clear record of open- and closed-system behavior and fluid sources. To utilize stable isotope compositions for this purpose, estimates of vein formation temperatures are required. In some cases, veins and shear zone rocks (mélangé) are clearly out of isotopic equilibrium with the more coherent (less deformed) host rocks and an external fluid composition and source can be obtained, given estimates of temperatures during the metasomatism (e.g., amphibolite unit in the Catalina Schist; [Bebout, 1991a](#)). Stable isotopes can also be homogenized over significant volumes of rock, consistent with fluid communication (mixing) over such scales and perhaps large-scale fluid mobility (see evidence for oxygen- and nitrogen-isotope homogenization in [Bebout, 1991b, 1997](#)). In contrast with these observations, [Barnicoat and Cartwright \(1995\)](#) and [Cartwright and Barnicoat \(1999\)](#) used oxygen-isotope data for metabasaltic rocks, including pillow basalts, and suggested that fluid

flow was extremely restricted, likely channelized, resulting in the preservation of oxygen-isotope signatures of seafloor hydrothermal alteration. These observations are consistent with those of other studies in which closed-system behavior was proposed in either metasedimentary or mafic compositions (e.g., [Getty and Selverstone, 1994](#); [Nadeau et al., 1993](#); [Henry et al., 1996](#); [Busigny et al., 2003](#)). The preservation of low- $\delta^{18}\text{O}$ signatures related to near-surface processes in UHP rocks in China attests to the ability of deeply subducted rocks to retain their presubduction isotopic compositions despite extensive metamorphic recrystallization (see [Rumble and Yui, 1998](#); [Zheng et al., 1998](#)), indicating limited or no infiltration of external fluids or isotopic exchange with the mantle during subduction. Stable isotope behavior similar to that observed for a Western Alps transect (including the Schistes Lustrés, Cottian Alps; see [Henry et al., 1996](#)), showing similarity in vein and host-rock isotopic compositions for the same minerals, was interpreted by [Sadofsky and Bebout \(2004b\)](#) for data from the Franciscan Complex to be the

result of transport of fluid through vast expanses of similar rock, resulting in apparent internal/local control.

[Hermann et al. \(in press\)](#) emphasized that the trace-element concentrations of veins in HP and UHP metamorphic rocks cannot be used as indicators of element mobility, other than in an extremely qualitative way. They stressed that one must use mineral-fluid partitioning data to estimate fluid compositions from vein trace-element concentrations. [Figure 17](#) presents one intriguing example of vein–host-rock relations in a HP eclogite from Monviso, Italy (see studies of the same locality by [Philippot and Selverstone, 1991](#); [Nadeau et al., 1993](#); [Rubatto and Hermann, 2003](#)). In this sample, garnet growth depleted the rock in HREE. Thus, omphacite included in the garnet has higher HREE, reflecting its growth before the majority of the garnet grew, whereas omphacite in the matrix is strongly depleted in HREE, due to its crystallization following garnet growth. Omphacite occurring in a vein in this same sample also has depleted HREE and may reflect control of vein chemistry by

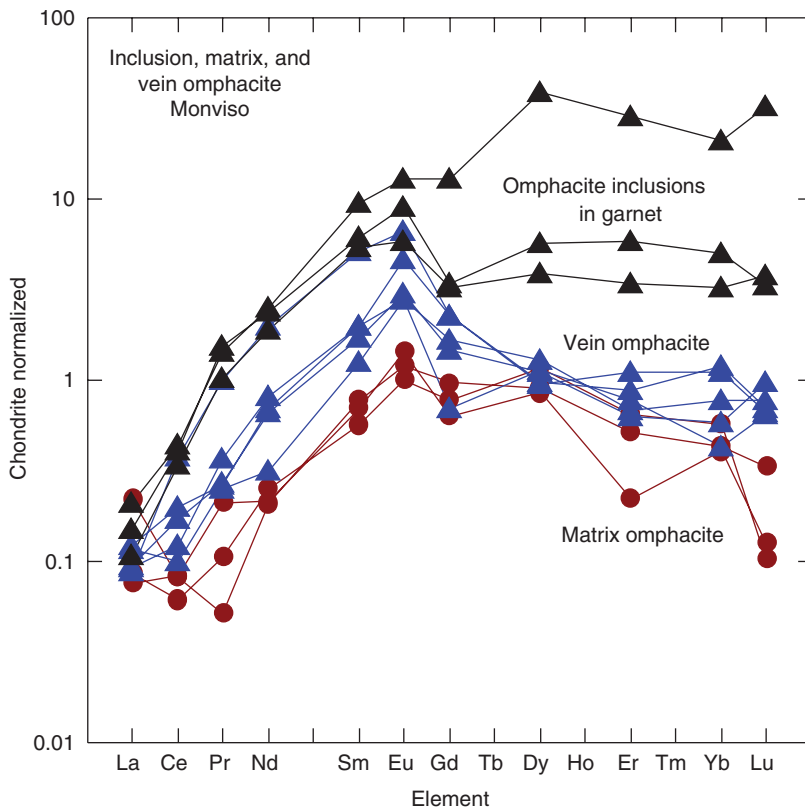


Figure 17 REE plots (normalized to chondritic values of [McDonough and Sun, 1995](#)) for omphacite in Monviso garnet-clinopyroxene metagabbros and omphacite in a vein in the same sample. Note that the REE pattern for the vein omphacite more closely resembles the pattern for omphacite in the matrix outside garnets and reflecting HREE depletion by garnet growth (data from [King et al., 2004](#); [King, 2006](#)), presumably related to relatively late-stage production of this vein.

the host-rocks after garnet growth. Rubatto and Hermann (2003) also presented trace-element data for veins in mafic rocks from this locality, and Hermann *et al.* (in press) calculated fluid compositions using the trace-element concentrations of vein omphacite and previously published partition coefficients (from Green and Adam, 2003). The calculated fluid had relatively elevated concentrations of Cs, Rb, Ba, Sr, and Pb, but the concentrations of most other elements were below 1 ppm.

Growing, but still modest, numbers of strontium-, neodymium-, lead- (and Re–Os, Lu–Hf) isotopic studies of HP and UHP mafic rocks provide further constraints on the sources of trace-element enrichments observed in these rocks relative to their protoliths. They also can provide insights into the degrees of open- versus closed-system behavior, both on the seafloor and during subduction-zone metamorphism (e.g., Nelson, 1995; Becker, 2000; Lapen *et al.*, 2003; John *et al.*, 2004). Relatively few studies have evaluated isotope records of fluid–rock interactions at scales larger than the hand-specimen or outcrop scale. Strontium-, neodymium-, and lead-isotope data for mafic blocks (and in some cases, their metasomatic rinds) in California tectonic mélange are interpreted as reflecting varying combinations of seafloor alteration, metasomatic interactions with mélange matrix, and possible IAB protoliths (see Nelson, 1995; Saha *et al.*, 2005).

Variations in fluid inclusion compositions at small scales are consistent with local-scale exchange between the fluids and rocks during or after their formation and possible decrepitation (see Philippot and Selverstone, 1991; Gao and Klemd, 2001; Hermann *et al.*, in press). Touret and Frezzotti (2003) summarize the record of fluid–rock interactions in subduction zones using fluid inclusions. Recently, trace-element analyses of individual inclusions have provided constraints on trace-element mobility, at least on the local scale (see Scambelluri *et al.*, 2004a), and fluid-inclusion salinities are directly relevant to discussions of chlorine cycling (see Philippot *et al.*, 1998). In a number of studies, at least parts of the fluid-inclusion record are directly associated with exhumation history (e.g., El-Shazly and Sisson, 1999; Franz *et al.*, 2001; Fu *et al.*, 2002).

3.20.5.8 Prograde Chemical Changes and Open- versus Closed-System Behavior

Because HP and UHP metamorphic suites experience protracted prograde and exhumation paths, with exhumation commonly strongly

overprinting the prograde assemblages, it is often necessary to identify ways to distinguish the mineral assemblages and textures and geochemistry associated with these two histories. One approach to identifying chemical change that can be directly associated with prograde subduction-zone history involves the exploitation of porphyroblast mineral inclusions and chemical and isotopic zoning. Garnet porphyroblasts are thought to experience slow volume diffusion and thus preserve prograde records through even protracted HT exhumation histories (these phases can also contain useful mineral inclusions; see King *et al.*, 2004; cf. Kurahashi *et al.*, 2001). Figure 18 demonstrates one way of doing this, by examining core-to-rim major and trace-element (and mineral inclusion) variations in garnets in UHP and metabasaltic rocks at the Lago di Cignana locality (from King *et al.*, 2004; King, 2006). In metasedimentary samples from this locality, highly overprinted by exhumation-related mineral assemblages, these records in phases such as garnet and tourmaline are the only remaining geochemical signal of the prograde history (see discussion in Bebout and Nakamura, 2003; Bebout *et al.*, 2004). However, the overprinting in mineral assemblages does not necessarily imply that the rocks were open systems during exhumation (see Bebout *et al.*, 2004).

Obviously, one of the keys to understanding any whole-rock geochemical change is the establishment of open- or closed-system behavior during various stages of metamorphism, including the exhumation stage. This can be complicated greatly by the heterogeneities in likely protoliths (see above) and by recrystallization and overprinting related to exhumation (see discussion for the Schistes Lustrés and Lago di Cignana metasedimentary rocks by Bebout *et al.*, 2004). As noted above, metasomatic rinds on blocks in ultramafic or sedimentary mélange provide one more clear record of element mobility during HP and UHP metamorphism. Another involves the use of ratios among elements of varying fluid mobility that are strongly sequestered into the same mineral phase (e.g., K/Cs and Rb/Cs in micas) to effectively normalize whole-rock heterogeneity (see Bebout and Fogel, 1992; Bebout *et al.*, 1999; see Figures 11 and 13).

Others have tested the degree to which the mineral phases in HP and UHP rocks fall on mineral isochrons (Glodny *et al.*, 2003; John *et al.*, 2004; Usui *et al.*, 2006; discussion in Lapen *et al.*, 2003). It is not clear how sensitive a measure of open-system behavior this type of test can be; Glodny *et al.* (2003) suggested that eclogitic rocks preserve their Rb/Sr isotopic signatures as long as they are devoid of

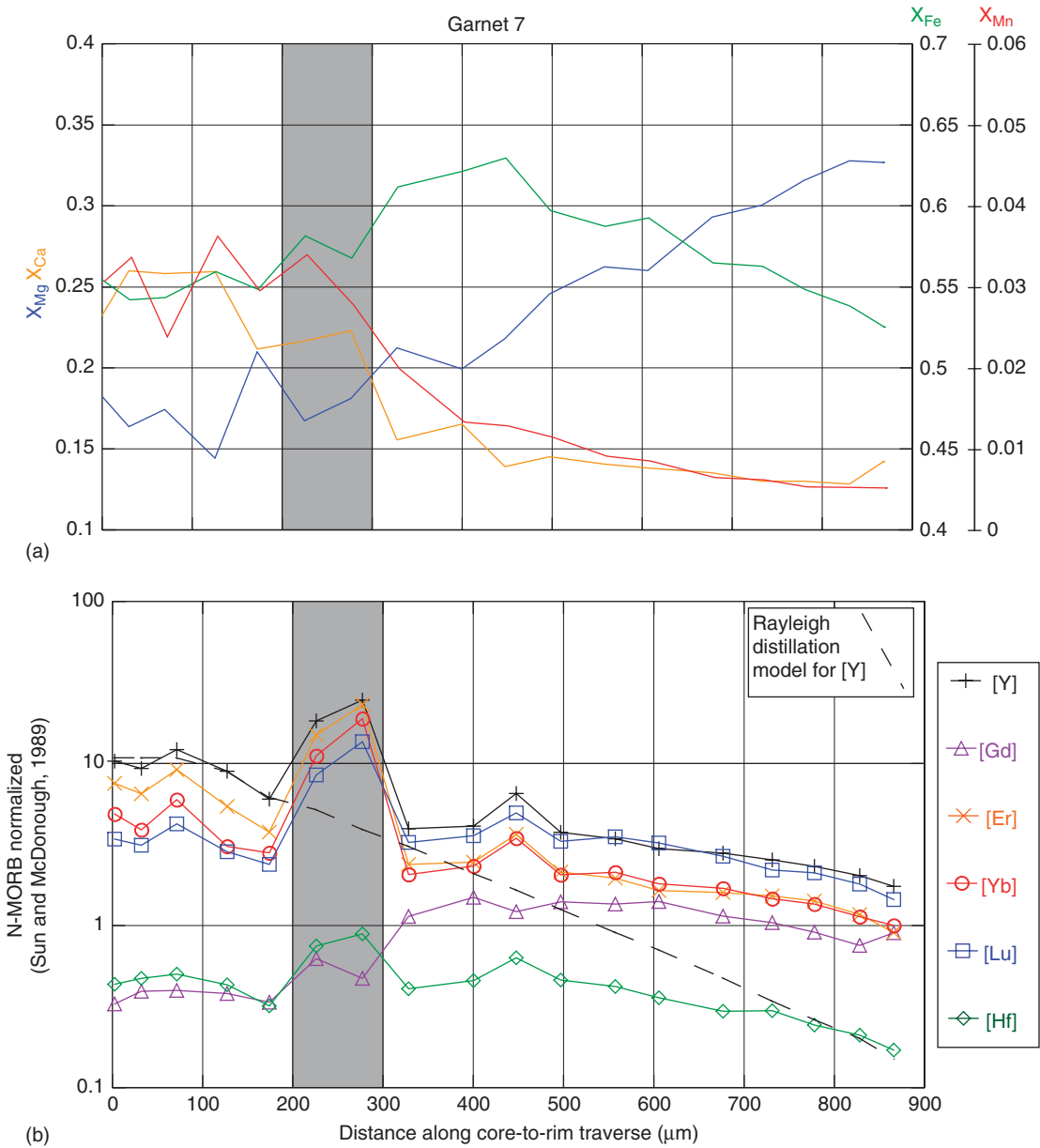


Figure 18 Major and trace-element zoning in a core-to-rim traverse (rim to the right) in a garnet in UHP metabasalt from Lago di Cignana (from King *et al.*, 2004; King, 2006; see similar approach of Usui *et al.*, in press). Note the anomaly in both major element (a) and trace-element (b) compositions that King *et al.* (2004) attribute to a prograde metamorphic reaction involving breakdown of clinozoisite and titanite to stabilize grossularite and rutile (see discussion by Skora *et al.*, in press). Trace-element concentrations are normalized to N-MORB values of Sun and McDonough (1989).

free fluids and that fluid–rock interactions cause Sr redistribution. Usui *et al.* (2006) suggested that xenolithic eclogites, in which lawsonite breaks down to zoisite, released fluids that led to strontium–neodymium–lead isotopic reequilibration. In contrast, jadeite–clinopyroxenite xenoliths that initially lacked lawsonite or significant amounts of zoisite, did not experience this release of fluid and thus preserve older ages.

3.20.5.9 Mineral Chemistries of HP and UHP Suites

Recently published microanalytical work highlights the value of obtaining chemical and isotopic data at the single-mineral (and intracrystalline) scales using microanalytical methods (e.g., SIMS or laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS)). Such work allows recovery of

mineral–mineral partitioning data for individual trace elements and isotopes of interest. It also allows exploitation of disequilibrium features such as porphyroblast chemical/isotopic zoning, and the chemical compositions of mineral inclusions in porphyroblasts, and evaluation of whole-rock effects of exhumation by analyses of prograde and exhumation-related parageneses identified based on textural evidence (see Zack *et al.*, 2001; Spandler *et al.*, 2003, 2004; Bebout and Nakamura, 2003; King *et al.*, 2004; Usui *et al.*, 2006; earlier work by Messiga *et al.*, 1995; Tribuzio *et al.*, 1996; Sassi *et al.*, 2000; Wiesli *et al.*, 2001).

Micas, particularly phengitic white micas, are the primary hosts of a number of trace elements that are of interest in subduction tracer studies (LILE, boron, nitrogen, and lithium, the latter for which clinopyroxene and chlorite are also major mineral hosts). White micas carry these elements to great depths in subduction zones (see Domanik and Holloway, 1996) in mafic, sedimentary, and ultramafic lithologies (for ultramafic mélangé, see Bebout, 1997; King *et al.*, 2006; see Figures 11–13). Paragonite (sodium-rich white mica) is also an

extremely important mineral host, particularly during exhumation (see Giorgetti *et al.*, 2000; Poli and Schmidt, 1997; Zack *et al.*, 2001), incorporating elements such as boron and strontium (Bebout *et al.*, 2004). Studies by Moran *et al.* (1992), Bebout and Fogel (1992), Bebout *et al.* (1993, 1999, in press), Domanik *et al.* (1993), Zack *et al.* (2001), and Busigny *et al.* (2003), among many others, demonstrate that the whole-rock budgets of LILE, boron, and nitrogen, are nearly completely contained within white micas.

A number of other phases can exert strong control over whole-rock trace-element budgets. First, lawsonite and zoisite/clinozoisite are extremely important hosts for LREE and strontium (Okamoto and Maruyama, 1999; Pawley, 1994, see Figure 19); thus, these phases are of extreme interest to those attempting to link mineral reactions in subducting lithologies with arc outputs (see King *et al.*, 2004; Moriguti *et al.*, 2004; Feineman *et al.*, in press; Chapter 3.17). Lawsonite in eclogite is preserved in only a very small number of suites, as it requires relatively cool (and/or rapid) exhumation trajectories (see recent reports of

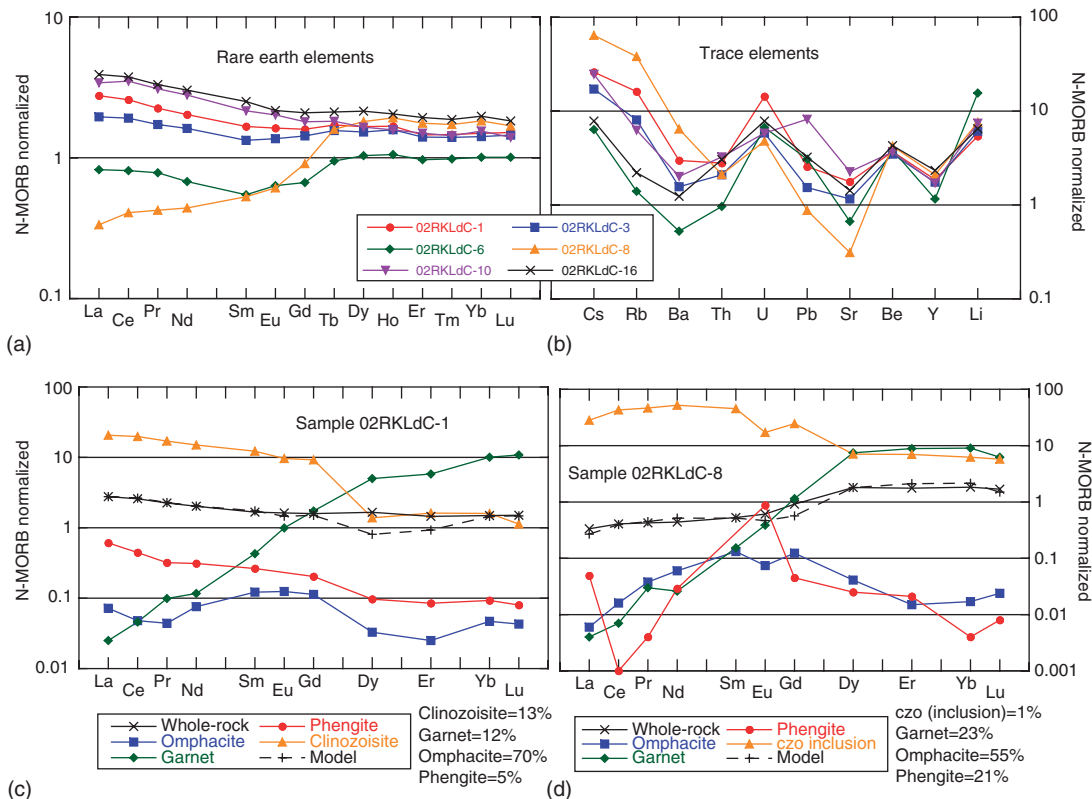


Figure 19 Bulk rock REE and other trace-element concentrations of Lago di Cignana UHP metabasaltic samples ((a) and (b)), both normalized to N-MORB of Hofmann (1988), and ((c) and (d)) mass balance of REE in two of these samples using mineral compositions and modes to reconstruct the whole-rock REE pattern. Data are from King *et al.* (2004) (also see King, 2006).

such rocks by Zack *et al.*, 2004; Altherr *et al.*, 2004; Usui *et al.*, 2006; Whitney and Davis, 2006; Tsujimori *et al.*, in press). At the Lago di Cignana locality, which experienced a relatively low-temperature exhumation P - T path (see path in Figure 6), lawsonite that is inferred to have been stable in HP/UHP mineral assemblages is pseudomorphed by intergrowths of orthojoisite, paragonite, and quartz (Reinecke, 1998). Usui *et al.* (2006) reported lawsonite, both as inclusions in garnet and as matrix phases, in xenolithic eclogites from the Colorado Plateau, which they interpret as being fragments of the subducted Farallon plate (see Usui *et al.*, 2003). Zoisite and clinozoisite are comparatively common in HP/UHP mafic (and sedimentary) lithologies (e.g., Brunsmann *et al.*, 2000, 2001). Figure 19 demonstrates the strong relationship between whole-rock strontium concentration and the modal abundances and strontium concentrations of clinozoisite for a suite of UHP eclogites from Lago di Cignana (data from King *et al.*, 2004; King, 2006; see similar data for other suites in Spandler *et al.*, 2003; Usui *et al.*, 2006).

Garnet in HP and UHP metamorphic rocks exhibits characteristic enrichments in HREE, in many cases dominating the whole-rock budget for these elements (see Figure 19). Rutile generally contains most of the niobium and tantalum present in the rock (Sorensen and Grossman, 1989; Zack *et al.*, 2002; Barth *et al.*, 2001; Spandler *et al.*, 2003). Omphacite accounts for much of the lithium in eclogites (Zack *et al.*, 2002; King *et al.*, 2004), and up to 100 ppm lithium in cores of garnet has been reported for some Cignana metasedimentary rocks in which the other primary lithium hosts are phengite and paragonite (Bebout *et al.*, 2004). Sorensen and Grossman (1989) (also see Sorensen, 1991) demonstrated the strong impact that small modal amounts of allanite can have on LREE budgets in garnet-amphibolites (also see Spandler *et al.*, 2003).

3.20.5.10 Forearc to Subarc: Summary and Outstanding Questions

The previous sections provide a look at the geochemical consequences of important mineral reactions during subduction across the forearc geochemical “filter,” and this allows insight regarding what the inventory of various trace-element and isotopic tracers is beneath the volcanic front, i.e., the geochemical menu available for addition by various “fluids” to the subarc mantle, which is addressed in the next

section. To sum up:

1. Consensus is developing that, in the relatively cool subduction-zone conditions predicted by thermal models for most modern subduction zones, subducting sediments (and probably also oceanic crustal rocks) can largely retain their inventories of even the more fluid-mobile elements, to at least 90 km (Lago di Cignana; Busigny *et al.*, 2003; Bebout *et al.*, 2004). In cases where young, warm oceanic lithosphere is being subducted (e.g., Cascadia; Kirby *et al.*, 1996), related to ridge-trench encounters, and in the Archean (see Staudigel and King, 1992; Foley *et al.*, 2003; Martin, 1986), higher geothermal gradients may generate greater forearc devolatilization leading to greater loss of fluid and fluid-mobile elements to the mantle wedge. The data for HP and UHP eclogites in Figures 7 and 8 indicate that a number of the elements of greatest interest to those studying arcs are actually enriched rather than lost, certainly arguing against any strong depletions related to prograde metamorphism to depths of up to ~90 km (cf. Chalot-Prat *et al.*, 2003; Spandler *et al.*, 2004; John *et al.*, 2004; Marschall *et al.*, 2006; see the contrasting conclusion by Becker *et al.*, 2000).
2. Exhumation paths can dictate the extent to which prograde chemical history is preserved in HP and UHP suites, and thus the usefulness of these suites for study of subduction-zone chemical cycling (see the great variability in exhumation paths in Figure 6). Warmer exhumation paths, in some cases producing peak temperatures after significant decompression (e.g., path for Adula nappe; from Jolivet *et al.*, 2003; exhumation paths for some rocks in the Dabieshan) increase the likelihood of significant overprinting during exhumation. Whether prograde parageneses and chemical records can be extracted must be considered on a suite-by-suite basis (e.g., for Trescolmen, see Zack *et al.*, 2001, 2002). Lawsonite-eclogites in which lawsonite has escaped decompression-related replacements (such as those experienced by the UHP rocks at Lago di Cignana; see Reinecke, 1998; van der Klauw *et al.*, 1997) are certainly prime candidates for detailed study of prograde reaction and chemical histories (Zack *et al.*, 2004).
3. Eclogites may experience closed-system metamorphism, but protolith heterogeneity prohibits identification of any minor element loss during devolatilization, and some eclogites could have had relatively “dry” protoliths that did not experience alteration on the seafloor (see Chapter 3.15). It is as yet

unclear whether it is possible to lose very small amounts of fluids and trace elements, over large volumes of subducting rocks, to produce the fluid and trace-element budget in the mantle wedge partly delivered toward the surface in arcs. Such loss could easily be obscured in the large protolith heterogeneity incorporated into any study of trace-element loss—in studies comparing higher-grade rocks with lower-grade or unmetamorphosed equivalents, only the extremely fluid-mobile elements (boron, cesium, arsenic, and antimony, for the Catalina Schist metasedimentary suite) show a clear record of whole-rock loss. A mass balance of this type, involving calculation of element loss using published partition coefficients, and evaluating the extents of loss that could be achieved without observing them, has not yet been conducted (see the brief consideration of this problem for boron and beryllium and B/Be of released fluids in [Bebout *et al.*, 1993](#); the analysis of the Catalina Schist LILE systematics by [Zack *et al.*, 2001](#)). Another question relates to whether more pronounced trace-element loss from such rocks, mostly concentrated in zones of higher fluid flux (see [John *et al.*, 2004](#); [Spandler *et al.*, 2004](#); see the discussion of the slab–mantle interface and devolatilization models below), could produce sufficient trace-element mobility to satisfy the arc record of slab additions.

4. Veins in many cases appear to reflect only local-scale element redistribution and it is unknown whether larger-scale removal of fluid-mobile elements can occur in subducting slabs. Although there is, in some cases, clear demonstration that fluid–rock interactions were relatively local-scale in relatively closed systems (e.g., [Philippot and Selverstone, 1991](#); [Getty and Selverstone, 1994](#); see [Scambelluri and Philippot, 2001](#)), some open-system behavior may occur at/near peak P – T conditions or along the prograde P – T path. Relatively, small fluid fluxes within large masses of chemically similar rock can be difficult to document using trace elements and stable isotopes and tracts of rock that contain vein systems in local equilibrium with host-rocks ([Gray *et al.*, 1991](#); [Henry *et al.*, 1996](#); [Sadofsky and Bebout, 2004b](#)) do not preclude infiltration by externally derived fluids. Integrated over large volumes of subducting sedimentary and mafic rocks, relatively small fluid fluxes could result in sufficient element flux to explain volcanic arc compositions. Larger-scale fluid and element transfer appears to be concentrated along zones of structural weakness (e.g., fractures, *mélange*), likely resulting in the disproportionate

influence of such zones on the chemical characteristics of any fluids traversing the slab–mantle interface beneath arcs.

5. The geochemical significance of *mélange* at depth in subduction zones is not clear. The scarcity of appropriate exposures has made it difficult to evaluate the volumetric significance of *mélange* zones at depth along the slab–mantle interface. Zones of low seismic velocity at or near the top of the subducting oceanic lithosphere may consist of extensively hydrated assemblages (see [Abers, 2000](#)); alternatively, they may represent hydrated hanging wall lithologies. The generation of layers rich in hydrous minerals, perhaps in part a mechanical mixing zone, could also promote aseismic behavior at great depths in subduction zones ([Peacock and Hyndman, 1999](#)). Further attention should be paid to *mélange* zones, in field, geophysical, and theoretical studies, to evaluate their potential for producing deep subduction-zone “fluids” with hybridized mafic–sedimentary–ultramafic compositions.

3.20.6 THE DEEP FOREARC AND SUBARC SLAB–MANTLE INTERFACE

Relatively few detailed geochemical studies have thus far been conducted on UHP rocks directly representing the slab–mantle interface at depths corresponding to those beneath and across arcs (see compilation in [Figure 6](#)), largely leaving us to speculate regarding the structural evolution and reaction histories, and related production of “fluids,” in slab and sediments subducted to these depths. [Figure 20](#) presents a conceptual model for forearc to subarc processes at/near the slab–mantle interface from [Breeding *et al.* \(2004\)](#) (see similar sketches by [Bebout and Barton, 1989, 2002](#); [Hermann *et al.*, in press](#)). It is likely that the slab–mantle interface is a region of high, but heterogeneous, fluid flux. There are abundant devolatilization (for most margins, particularly dehydration) reactions in mafic, sedimentary, and even ultramafic rocks capable of producing large amounts of fluid (see Chapter 3.17), and arc lava geochemistry bears testament to the presence of large amounts of H₂O-rich “fluid” beneath arcs. Active deformation should lead to heterogeneous fluid transport along zones of structural weakness. Relatively coherent tracts of mafic HP and UHP rocks for which limited, or no, fluid mobility is proposed (e.g., metamorphosed Jurassic ophiolite in the Alps), likely represent the stronger, less permeable

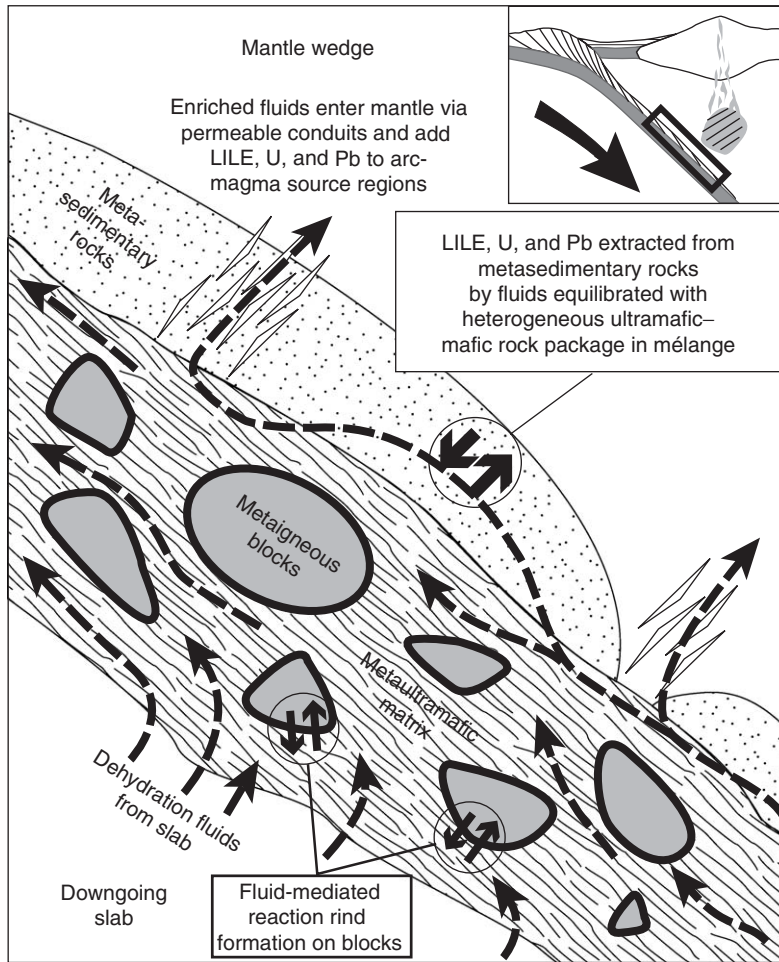


Figure 20 A view of the slab–mantle interface region (from Breeding *et al.*, 2004; also see sketches by Bebout and Barton, 1989, 2002; Hermann *et al.*, in press). See text for discussion. Reproduced by permission of Geological Society of America from Breeding *et al.* (2004).

lithologies within a lithologic package characterized by strong contrasts in rheology and heterogeneous permeability structure (see discussions by Philippot, 1993; Philippot and Selverstone, 1991; Getty and Selverstone, 1994; Spandler *et al.*, 2003, 2004; Chalot-Prat *et al.*, 2003; for isotopic evidence for limited mobility in coherent rocks in the Catalina Schist, see Bebout, 1991b; Bebout and Fogel, 1992). Zones of mixing among sedimentary and hydrated mafic and ultramafic rocks likely exist along the slab–mantle interface. Roughness in the subducting slab, produced by seafloor and trench deformation and in the form of seamounts, would promote the off-scraping of mafic lithologies and incorporation into sedimentary–ultramafic mixing zones. The enhanced fluid flux in such zones would produce talc, chlorite, and amphibole, which are weak and easily deformed thus further enhancing fluid transport (see Peacock and Hyndman, 1999; Ague, in press). These zones of

preferential fluid flow would also be more intensely metasomatized, leading to their disproportionate representation in any “fluid” (hydrous 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 and leading to their incorporation into the mixing zones (Peacock and Hyndman, 1999; see Bebout and Barton, 2002).

If the upper-mantle section in subducting slabs is hydrated on the seafloor or in forearc regions (see Ranero *et al.*, 2005), far greater amounts of fluid could ascend into mixing zones at the slab–mantle interface (see Hermann *et al.*, in press). The H₂O-rich fluid produced by dehydration of these ultramafic lithologies will cause metasomatic exchange with disparate lithologies and drive decarbonation reactions

in more carbonate-rich systems (Gorman *et al.*, 2006), such as in the modern Central America and Banda convergent margins. In convergent margins where HP and UHP rocks are exhumed by later collision (Alps, Himalaya), mélangé zones are likely to be reactivated and strongly overprinted by fluid–rock interactions during exhumation, making them more difficult to identify and investigate for their prograde/peak metamorphic geochemistry. Thus, the more structurally intact, less-permeable lithologies tend to be the best preserved in these orogens, and consequently show less evidence for large-scale fluid flow. Blocks that are tectonically incorporated into mélangé zones provide a record of fluid and metasomatic processes at the slab–mantle interface, but unfortunately do not record processes operating in the subducting slab.

Zack *et al.* (2001) used published mica–fluid partitioning data (Melzer and Wunder, 2001) along with LILE concentrations of the Catalina Schist metasedimentary rocks to suggest that an external source of H₂O-rich fluid is required to produce the observed fractionations of element ratios in these rocks (particularly Cs/K). As illustrated in Figure 20, from Breeding *et al.* (2004), such fluid fluxing through metasedimentary rocks, which are either underplated to the hanging-wall or incorporated as tabular bodies in mélangé zones, is expected if large amounts of fluid ascend from dehydrating mafic and ultramafic rocks at depth in the subducting slab (see Ranero *et al.*, 2005).

The complexity of metasomatism along upward (and lateral) fluid flow paths into the mantle wedge immediately overlying subducting slabs is widely acknowledged and we have much to learn regarding the mineral–fluid reactions and resulting geochemistry that occur in this region (see discussion by King *et al.*, 2003). Studies of intact tracts (see Paquin *et al.*, 2004; Scambelluri *et al.*, 2006, and references therein), ultramafic xenoliths found (rarely) in arc volcanic rocks (Maury *et al.*, 1992; Schiano *et al.*, 1995; Laurora *et al.*, 2001; Widom *et al.*, 2003) and hydrated forearc mantle wedge in serpentinite seamounts (Ryan *et al.*, 1996; Benton *et al.*, 2001, 2004; Savov *et al.*, 2005) have yielded insights into the reactions and processes occurring in the wedge.

3.20.7 SLAB-ARC CONNECTIONS

3.20.7.1 Brief Discussion of the Geochemistry of Arc Basalts and Inferred Slab Additions

There is general consensus, based on the geochemistry of arc basalts and their differences

relative to various MORB compositions, regarding the most likely additions to arc source regions via “fluids” from the slab (see recent discussions by Pearce and Peate, 1995; Elliott, 2003; Tatsumi, 2005; Hermann *et al.*, in press; Chapters 2.11 and 3.18). Cesium, rubidium, radium, barium, thorium, uranium, potassium, the light REEs, lead, and strontium are enriched in arc lavas relative to MORB (Figure 2a; in some cases, also boron, lithium, ¹⁰Be; see Chapter 2.11; Pearce and Peate, 1995; Elliott, 2003, and references therein). In general, subducting oceanic crust is enriched in the elements that are also enriched in arc lavas relative to MORB, and various combinations of hydrous fluids, silicate melts, and supercritical liquids are called upon to transfer these elements into arc source regions. A smaller number of these elements (cesium, boron, arsenic, antimony, lithium, and lead) are regarded as being particularly “fluid-mobile” and likely to be either lost to hydrous fluids during forearc devolatilization or transported in hydrous fluids into arc source regions (see Moran *et al.*, 1992; Noll *et al.*, 1996; Leeman, 1996; Ryan *et al.*, 1995, 1996). Enrichments of other elements, in arc lavas, that appear to be less mobile in hydrous fluids (e.g., thorium and beryllium) are thought to require transport in a silicate melt (Johnson and Plank, 1999; for discussion of thorium immobility in hydrous fluids see Brennan *et al.*, 1995a). This dichotomy has led to the “sediments melt, oceanic crust dehydrates” conclusion reached in a number of studies of arc geochemistry.

The evidence for mobility of LILE elements such as Ba, Rb, Cs, and Sr, and possibly also U and Pb, demonstrated in studies of metasomatic rind formation, mélangé evolution, and evident in the data for metabasalts and metagabbros summarized in Figures 7 and 8, is certainly in general compatible with the “slab additions” of these elements invoked in studies of arc magmatism. The data of Becker *et al.* (2000), although complicated by the lack of control on protoliths, indicate LILE (particularly K, Rb, and Ba) loss during eclogite-facies metamorphism, which may for some samples reflect melt removal, as a number of the samples these authors analyzed have peak *P–T* near or above the wet solidus. Silicate melts (and supercritical liquids; see Kessel *et al.*, 2005; Hermann *et al.*, in press) are presumably more effective than hydrous fluids in removing elements such as the LILE (particularly rubidium, barium, and strontium; see discussion on granulite potassium, rubidium, and cesium by Hart and Reid, 1991).

From an arc geochemist’s perspective, the forearc can be viewed as a metamorphic “filter” that can either prevent or allow the

retention of relatively fluid-mobile components to greater depths in the subduction zone (for noble gases, forearc metamorphism may represent a “barrier” to deep recycling, as proposed by Staudacher and Allègre, 1988). Studies of metasedimentary rocks appear to demonstrate remarkable retention of elements such as boron and cesium to depths of up to 90 km in relatively cool subduction zones (Bebout *et al.*, 1999, 2004; Busigny *et al.*, 2003; and discussion above). With the exception of the studies by Becker *et al.* (2000) and Arculus *et al.* (1999), which were limited somewhat by insufficient consideration of protolith heterogeneity, the previous work on HP/UHP metabasaltic and metagabbroic rocks similarly points to the retention of many of the elements of interest as “slab tracers” to depths beneath the volcanic front (~100 km or more; Gill, 1981; Chapter 3.17; Figures 7 and 8). The correlations between concentrations of certain trace elements (particularly potassium, barium, strontium, and thorium) in subducting sediments with average concentrations of these elements in the overlying arc lavas (Plank and Langmuir, 1993; Plank, 2005) are also in general compatible with the retention of the bulk of these elements (at least in the sediments) to depths beneath arcs.

For metabasaltic rocks, the depth to the blueschist–eclogite transition (which is strongly dependent on the thermal structure of a given subduction zone), and the breakdown of lawsonite within the eclogite facies, likely play key roles in the geochemistry of slab fluids (Peacock, 2003; Hacker *et al.*, 2003a, b; see discussion of fluids at this transition by Manning, 1998). However, the rather large number of recently published slab *P–T* paths, with various assumptions made regarding frictional heating and, particularly, mantle wedge viscosity, leaves one with the impression that it is not possible to pinpoint the temperature of the slab–mantle interface in any given arc (see Peacock *et al.*, 2005). Some recent models suggest that the slab–mantle interface is, for a number of margins, warm enough for sediment melting and nearly warm enough to approach the wet solidus of altered basalt (Peacock *et al.*, 2005). Peacock (2003) demonstrates that the blueschist (or for the hotter Nankai subduction zone, the greenschist)–eclogite transition, for rocks at or near the slab–mantle interface, could occur at depths ranging from ~50 to 110 km (see Figure 3). The majority of the eclogites that have been investigated for their geochemistry have estimated peak metamorphic pressures within, but at the lower end of this range (peak pressures corresponding to ~50–90 km, i.e., mostly not in the coesite

stability field; see Figure 6). Models of sediment devolatilization also indicate significant dehydration and decarbonation in the forearc (Kerrick and Connolly, 2001; Gorman *et al.*, 2006), with an apparent locus of fluid loss in the 60–80 km depth range.

Arc lavas overlying cooler subducting slabs (e.g., Marianas and Kuriles) have higher concentrations of Cs, B, As, and Sb than the arc lavas from “warmer” subduction zones (e.g., for Cascadia, Kirby *et al.*, 1996; discussion of arc data by Noll *et al.*, 1996). This is manifest in the arc lavas from cool subduction zones showing higher ratios of these elements to less fluid-mobile elements having similar incompatibility during partial melting in the mantle wedge (e.g., B/Be, Cs/Th, As/Ce, and Sb/Ce; see Bebout *et al.*, 1999; Chapter 2.11). The lower ratios in margins such as Cascadia are presumed to reflect the removal of these elements via metamorphic devolatilization in the relatively warm forearc (see Bebout *et al.*, 1999; Figure 11d), making these elements unavailable for delivery into the corresponding arc.

3.20.7.2 Cross-Arc Variations

3.20.7.2.1 Devolatilization

The cross-arc variations observed in some isotope and trace-element ratios (see review by Chapter 2.11; Figure 21) provide tantalizing evidence that slab metamorphism results in the “distillation” of some components (resembling the losses in warmer units of the Catalina Schist), as it traverses the subarc region. Such observations lead to hypotheses that can be tested by further work on UHP metamorphic suites. These across-arc variations have been interpreted to diminishing fluid additions, changing fluid compositions, and/or changes in the proportions of hydrous fluids and silicate melts toward the back-arc (see discussion in Bebout *et al.*, 1999). The recently proposed transitions in the physical and chemical transport properties of “fluids” from subducting slabs (see Kessel *et al.*, 2005; Hermann *et al.*, in press) will need to be considered in future geochemical field studies of UHP suites that potentially represent the residues of fluid and element removal at >100 km depths in subduction zones. This could be achieved by investigating UHP suites straddling and above the wet solidi in pressure and temperature, and representing a range of depths consistent with those of the slab–mantle interface across arcs, and attempting to identify any differing styles of element loss (or gain) related to interactions with these “fluids” of differing types.

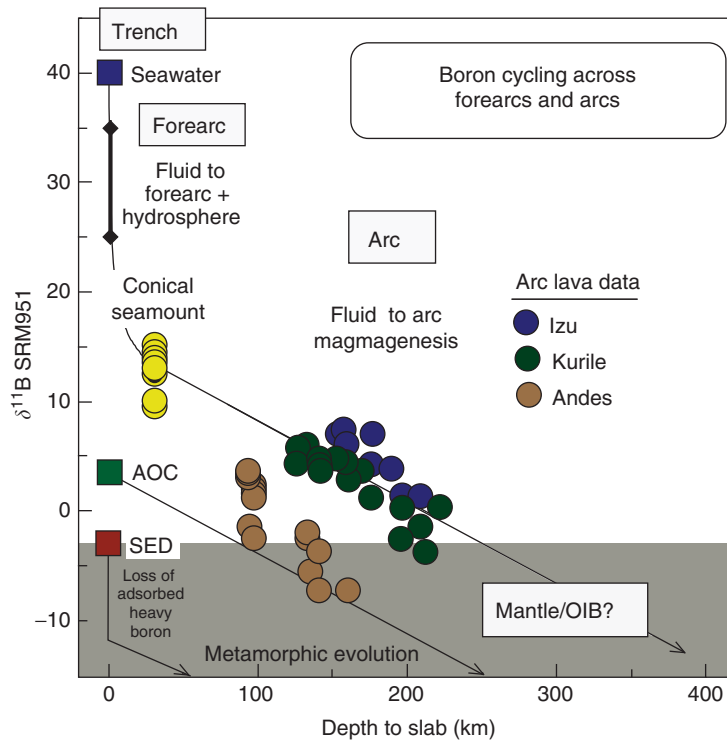


Figure 21 Cross-arc boron-isotope evolution, taking into account compositions of near-trench fluids, seawater, altered oceanic crust, and seafloor sediment (before and after loss of high- $\delta^{11}\text{B}$ adsorbed B) (Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Rosner *et al.*, 2003), and approximate trends in $\delta^{11}\text{B}$ (arrows) with prograde metamorphism of AOC and sediment (from the 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. Modified with permission from Benton *et al.* (2001).

3.20.7.2.2 Boron and lithium isotopes

Among the tracers showing variation across arcs, boron and lithium and their isotopes are particularly noteworthy. Because both are fluid-mobile, these elements are thought to be great “fluid tracers,” but with different fluid-mineral partition coefficients (see Chapter 2.11; Marschall *et al.*, 2006). Boron is extremely incompatible in the mantle wedge and, in arcs, it provides a record of very recent boron flux off the slab (Figure 21), whereas lithium is believed to be more compatible and to reside in the mantle wedge for longer periods of time (see Tomascak *et al.*, 2002; Benton *et al.*, 2004; Chapter 2.11). This difference in compatibility in the mantle wedge explains why lithium does not show cross-arc variations as pronounced as those for boron (Moriguti *et al.*, 2004; Chapter 2.11). Moreover, a boron-rich phase, tourmaline, occurs in HP and UHP metasedimentary suites (Nakano and Nakamura, 2001; Bebout and Nakamura, 2003), whereas lithium has no analogous phase in which it is a primary constituent; this likely produces a differing overall behavior in subducting slabs in

response to complex mineral reactions. Wunder *et al.* (2005, 2006) published experimentally determined boron-isotope fluid-mineral fractionation factors that appear wholly consistent with the variations observed across arcs, and lithium-isotope fractionations that appear to be consistent with the shifts to lower $\delta^7\text{Li}$ observed for eclogites as a result of devolatilization (Zack *et al.*, 2003).

Figure 21 presents some current thinking regarding trench-to-subarc (and beyond) cycling of boron, and associated boron-isotope shifts (from Benton *et al.*, 2001). This model sets forth some testable hypotheses regarding the evolution of boron concentrations and isotopic compositions in seafloor rocks subducted beneath arcs, beginning with very early loss of isotopically heavy adsorbed boron in forearc sediments (see You *et al.*, 1995). According to this model, isotopically heavy boron is lost from subducting rocks (presumably both AOC and sediment; see Bebout and Nakamura, 2003), more significantly in some margins than others (depending on thermal evolution), and this loss is likely to be primarily from micas (Bebout *et al.*, 1993). Recently published

fractionation factors for boron isotopes between mica and fluid (Wunder *et al.*, 2005) confirm the previous expectations regarding the direction and magnitude of this fractionation (see Peacock and Hervig, 1999). Calculations of boron-isotope evolution for forearc sedimentary and mafic rocks, with boron housed in mica, were presented by Bebout and Nakamura (2003; also see Nakano and Nakamura, 2001 and Marschall *et al.*, in press), along with evidence from isotopically zoned tourmaline for this prograde evolution. At greater depths beneath arcs, boron-isotopic evolution (and boron cycling) should continue to be strongly dictated by reactions involving mica (and tourmaline), whether they are in equilibrium with hydrous fluids, silicate melts, or supercritical liquids; this processing beyond the forearc should result in a further decrease in $\delta^{11}\text{B}$ (observed for a number of across-arc suites; see Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Rosner *et al.*, 2003; Figure 21). Based on aqueous fluid-mineral partitioning experiments, Brenan *et al.* (1998) calculated that B/Be and B/Nb should both be reduced considerably by the time the slab is subducted to 200 km, providing a possible explanation for observed cross-arc trends in these ratios.

The lithium cycle in convergent margins, starting on the seafloor with early diagenetic processes, has recently been discussed by Moriguti and Nakamura (1998), Tomascak *et al.* (2002), Benton *et al.* (2004), Elliott *et al.* (2004), and Magna *et al.* (in press). Benton *et al.* (2004; also see Tomascak *et al.*, 2002) suggested that, whereas B/Be and boron isotopes in arc lavas record the latest fluid additions to the subarc mantle, lithium isotopes reflect the aggregate longer-term modification and heterogeneity in the mantle source—this factor smoothes or “erases” the subduction input signal for lithium isotopes (see Wunder *et al.*, 2006). Zack *et al.* (2003) presented data for eclogites from the Alps that suggest shifts to lower δLi in these deeply subducted mafic rocks, which they related to metamorphic devolatilization. Lithium is generally thought to be more compatible in phases such as chlorite, the micas, and in eclogites, clinopyroxene (see Bebout *et al.*, 1999, in press). Bebout *et al.* (in press; also see Bebout and Fogel, 1992) documented little or no loss of lithium from metasedimentary rocks that experienced significant loss of boron, cesium, and nitrogen (data for white-mica boron and cesium in Figure 11). The model for fractionation set forth by Zack *et al.* (2003) for eclogites requires testing in studies of other suites, particularly suites for which there are better constraints on the fraction of lithium lost.

3.20.7.3 Carbon and Nitrogen Input and Arc Output

An example of the exciting synergy possible among studies of oceanic crustal inputs, subduction zone metamorphic rocks, and volcanic gas outputs is provided by the work on C–N cycling at the Costa Rica subduction zone. Recent work by Fischer *et al.* (2002), Hilton *et al.* (2002), Snyder *et al.* (2003), Shaw *et al.* (2003), and Zimmer *et al.* (2004) provide an assessment of the volcanic gas flux of carbon and nitrogen, including estimates of the proportions of end-member sources contributing to the gas compositions. Studies of AOC and sedimentary inputs to subduction zones and studies of metamorphic devolatilization (Bebout *et al.*, 1999; Sadofsky and Bebout, 2004a; Kerrick and Connolly, 2001; Li and Bebout, 2005) can be merged with the volcanic gas record to ascertain efficiencies of carbon and nitrogen return to the atmosphere through subduction zones. Studies of HP and UHP suites indicate that a considerable fraction of subducted carbonate (particularly when pure) is very deeply subducted (examples include Lago di Cignana, Schistes Lustres, and Dabieshan (Reinecke, 1998; Agard *et al.*, 2002; Mahlen *et al.*, 2005; Chapter 3.09). It appears that graphite is also quite stable; in the Catalina Schist, even partially melted rocks retain most of their sedimentary organic carbon as graphite (Bebout, 1995). Sadofsky and Bebout (2004a) and Li and Bebout (2005) discuss the large effect on calculated arc carbon and nitrogen return, relative to subduction inputs, when the estimates of C–N input are based on analyses of seafloor sediment just outboard of the Izu-Bonin and Central America trenches. For the Central America margin, Fischer *et al.* (2002) suggested that arc volcanic nitrogen output is approximately equal to the sedimentary subduction input of nitrogen, using estimates of sedimentary nitrogen concentration from Bebout (1995). Use of estimates of sedimentary nitrogen subduction input derived from study of the sedimentary section outboard of the Central American trench (at ODP Site 1039) indicates that arc return is nearer 50% of the sedimentary input (see Li and Bebout, 2005).

There are some indications that in relatively cool subduction zones, carbon- and nitrogen-isotope compositions of seafloor lithologies are preserved to at least 90 km depth. As noted above, the deeply subducted Schistes Lustres appear to preserve $\delta^{15}\text{N}$ like that of their seafloor protoliths (Busigny *et al.*, 2003), and in the Catalina Schist, only rocks subducted along warmer P – T paths show significant change in nitrogen-isotope composition (Bebout and Fogel, 1992). Carbonate-rich lithologies appear

to preserve seafloor-like carbon- and oxygen-isotope compositions, except in zones infiltrated by fluids from adjacent disparate lithologies, or where metasedimentary carbon reservoirs isotopically exchange during heating, resulting in evolving $\delta^{13}\text{C}$ (see discussion below; Busigny *et al.*, 2003). Studies of arc volcanic gases employing noble gases have estimated the proportions of carbon- and nitrogen-isotope sources for the gases using endmember isotopic compositions based on seafloor compositions shifted isotopically by metamorphism (see Hilton *et al.*, 2002). At present it appears that this approach is justified, although the shifts in $\delta^{15}\text{N}$ have thus far been documented only for HP metasedimentary rocks thought to have been metamorphosed along P - T paths warmer than those experienced in most modern convergent margins (the high-grade Catalina Schist metasedimentary rocks; Bebout and Fogel, 1992; Bebout *et al.*, 1999).

3.20.7.4 Other Stable Isotope Tracers (Oxygen, Hydrogen, and Chlorine)

It is generally accepted that the oxygen-isotope signatures of ocean-floor basalts are preserved through subduction-zone metamorphism, and conveyed into the deep mantle; however, the oxygen-isotopic compositions of mafic rocks in HP and UHP metamorphic suites can locally be modified by subduction-zone fluid-rock interactions (e.g., addition of sedimentary signatures, see above). Devolatilization is not expected to appreciably shift the oxygen-isotope composition of the rocks, as the majority of the oxygen reservoir in subducting rocks is retained in the residue. However, melting and dehydration of various lithologies (sedimentary, mafic, and ultramafic) could produce “fluids” of varying $\delta^{18}\text{O}$ that could be identifiable in studies of volcanic arcs. Based on oxygen-isotope compositions of olivine and plagioclase phenocrysts in arc basalts and basaltic andesites, Eiler *et al.* (2005) argued for varying contributions of low- $\delta^{18}\text{O}$, solute-rich aqueous fluids derived from dehydration of hydrothermally altered basaltic crust and partial melts of high- $\delta^{18}\text{O}$ sediments to the lavas of the Central American arc (see study of along-strike chemical variations by Carr *et al.*, 2003). Bindeman *et al.* (2005) obtained oxygen-isotope compositions for a suite of arc lavas, from various localities, previously hypothesized as reflect slab melting, and suggested that the $\delta^{18}\text{O}$ values of these lavas probably reflect varying degrees of slab and sediment melting, additions of slab-derived

aqueous fluids, or crustal contamination in the over-riding plate.

Bebout (1991a) suggested that the hydrogen-isotope compositions of hydrous minerals in the Catalina Schist metasomatic rocks could reflect the entrainment of seawater-like signatures to great depth via a complex hydration-dehydration cycle beginning on the seafloor, during fluid-rock interactions at mid-ocean ridges and during diagenesis (calculated δD ranges from -30‰ to 0‰ ; also see Magaritz and Taylor, 1976, who considered the possibility of deep seawater entrainment into subduction zones). Oceanic igneous rocks are hydrated and undergo hydrogen-isotope exchange on the seafloor over approximately the same temperature range at which hydrogen is released as H_2O in subduction zones. This could result in release of H_2O -rich fluids in subduction zones that have hydrogen-isotope compositions near those of seawater (Bebout, 1991a). Earlier work by Poreda (1985), and later work by O’Leary *et al.* (2002) invoke additions of “fluids” with δD heavier than the mantle values near -85‰ that appear to be attributable in some way to a multistage process of seafloor hydration (mafic or ultramafic) and subduction-zone dehydration or melting.

Chlorine-isotope studies, aimed at defining the ocean-mantle Cl subduction cycle, are still mostly on the horizon, with early studies mostly identifying the dominant reservoirs for Cl subduction, the magnitude of Cl flux at convergent margins and mechanisms of Cl mobility and release into arc lavas (see discussion by Sharp and Barnes, 2004). Insufficient work, other than that on fluid inclusions and shallower fluids in accretionary prisms (for the latter, see Spivack *et al.*, 2002), has been directed at the subduction-zone metamorphic pathway to greater depths in the forearc and beneath arcs (in response to metamorphic reactions in subducting sediment and oceanic crust) and its possible effects on the size and isotopic changes of Cl being added to arc source regions or the deeper mantle (see discussion by Hermann *et al.*, in press). In their study of seafloor serpentinites, Sharp and Barnes (2004) identified water-soluble and water-insoluble fractions of chlorine with somewhat different chlorine-isotope compositions, and suggested that the chlorine subduction flux in serpentinite in oceanic crust could be as much as twice that estimated by Ito *et al.* (1983), who took into account sediment and oceanic crust containing no serpentinite (also see Jarrard, 2003). A number of authors have argued for the large impact of serpentinite dehydration in the overall slab release of chlorine (Philippot *et al.*, 1998;

Scambelluri and Philippot, 2001; Sharp and Barnes, 2004).

3.20.7.5 The Nature of the Slab-Derived “Fluid” in Arc Magmas

As noted briefly above, it has been common for those researching slab additions to arc magmas to call upon varying combinations of hydrous fluid and silicate melts (with significant amounts of dissolved H₂O) as transport agents. Melts (generally of sediment) have been invoked to explain enrichments in Th relative to LREE and enrichments in light/middle REE and ¹⁰Be (subducted in only young seafloor sediment; see discussion in Chapter 3.18). Recent experimentally determined datasets for element partitioning among aqueous fluids (of varying chlorinity), hydrous melts, and “supercritical liquids” demonstrate the capability of these “fluids” to convey these trace elements from subducting slab-crust lithologies into the mantle wedge (e.g., Ayers and Watson, 1991; Brenan *et al.*, 1995b; Keppler, 1996; Tatsumi and Kogiso, 1997; Johnson and Plank, 1999; Kessel *et al.*, 2005). These experimental studies have produced compelling arguments that these “fluids” are capable of producing many of the distinctive signatures of arc magmatism (e.g., the low Ce/Pb and low-HFSE concentrations of arc lavas; see Brenan *et al.*, 1994, 1995a; Ayers and Watson, 1991).

Discussion of the physicochemical characteristics of the slab “fluid(s)” (see Manning, 2004) ties in with the recent development of thermal models of subduction, which indicate that the slab–mantle interface, containing sediments and uppermost AOC, could be at or near the wet solidus for both lithologies. A comparison of calculated peak metamorphic *P–T* for eclogites (see Figure 6) and recently published thermal models for subduction (see models from Peacock, 2003, in Figure 3) demonstrates that the peak *P–T* conditions for a number of UHP suites fall near or above the wet solidi, and geochemical work on such rocks can potentially yield insight regarding the nature of “fluids” produced from such rocks at these conditions (see Hacker *et al.*, 2005). Hermann *et al.* (in press) provide 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.*, 2005). More dilute aqueous solutions (e.g., present at the blueschist to eclogite transition at ~60 km depth) are regarded as being relatively ineffective in removing trace elements, based on experimentally derived partitioning data (see

Hermann *et al.*, in press), whereas 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 many of the specific enrichments invoked in studies of arc magmatism.

The Catalina Schist provides an unusual opportunity to examine evidence for partial melting of mafic and sedimentary rocks at amphibolite-facies conditions in a subduction zone (650–750 °C; 0.8–1.2 GPa; see Figures 6 and 9; Sorensen and Barton, 1987; Bebout, 1989; Bebout and Barton, 1993). Mafic blocks surrounded by largely metaultramafic mélange show migmatitic textures (Sorensen and Barton, 1987; Sorensen and Grossman, 1989), as do more coherent tracts of metagabbroic and metasedimentary rocks. Moreover, the mélange matrix contains plagioclase-rich (trondhjemitic) pegmatites. Because O–H isotopic data indicate infiltration of the mélange and the more permeable parts of the more coherent rocks by H₂O-rich fluids (Bebout and Barton, 1989; Bebout, 1991a), the amphibolite-facies unit appears to preserve evidence for mass transfer via both hydrous fluids and silicate melts, the latter represented by the pegmatites. This provides a possible analog to the models in which sedimentary rocks at or near the slab–mantle interface experience infiltration by fluids generated at greater depths, resulting in element stripping by hydrous fluids or silicate melts (see Breeding *et al.*, 2004; Hermann *et al.*, in press).

3.20.8 BEYOND ARCS

As discussed in Chapter 2.03, it has become relatively routine to associate certain geochemical signatures (high- μ ($\mu = ({}^{238}\text{U}/{}^{204}\text{Pb})_{t=0}$) (HIMU), enriched mantle (EM)-1 EM-2, and others) of the deep-mantle sampled by OIBs to varying combinations of subducted oceanic sediment, oceanic lithosphere, and oceanic island and plateau materials that may have experienced considerable ageing during long-term residence in the deep mantle (see Hart and Staudigel, 1989). These studies generally conclude that some subduction-zone chemical change is also required (Hart and Staudigel, 1989; Kelley *et al.*, 2005; Elliott *et al.*, 1999; Bach *et al.*, 2003; Chauvel *et al.*, 1995). A large amount of chemical change can be imagined as the result of complex dehydration and melting processes across deeper parts of the forearc and beneath arcs. The challenge in future studies is to identify these changes in exhumed HP and UHP rocks, and how these changes relate to the proposed transitions in subduction “fluids”

from more dilute aqueous solutions, to “transitional fluids,” then to hydrous silicate melts (see discussion by [Hermann *et al.*, in press](#)). The work thus far on metamorphic geochemistry in subduction zones has mostly been conducted on suites representing subduction to ≤ 100 km in P - T regimes dominantly generating hydrous fluids ([Figure 6](#)). It remains unclear whether certain element losses from subducting rocks over the full forearc to sub-arc depth range can produce appropriate chemically fractionated residues that match the source characteristics of OIBs ([Figure 1](#)). In particular, the role of supercritical liquids or silicate melts needs to be more thoroughly evaluated if these are shown to be important agents of slab flux beneath arcs (i.e., at >100 km depths). The greater LILE depletions in HP and UHP suites that have experienced partial melting ([Becker *et al.*, 2000](#); [Yamamoto *et al.*, 2002](#); LILE data for granulites in [Hart and Reid, 1991](#); also see [Hacker *et al.*, 2005](#), and a comparison of hydrous-fluid-rock and melt-rock partition coefficients by [Kessel *et al.*, 2005](#)) are a reminder that we must conduct further geochemical studies on UHP suites on or above wet and dehydration solidi ([Figure 6](#)).

It has long been recognized that low-temperature hydrothermal alteration on the seafloor shifts the $\delta^{18}\text{O}$ of shallow oceanic crust to higher values, and at greater depths and higher temperatures to lower values ([Gregory and Taylor, 1981](#)). This record of isotopic change can be preserved in HP and UHP metamorphic suites, suggesting that it can be conveyed to great depths in subduction zones without significant alteration (see [Cartwright and Barnicoat, 1999](#)). [Eiler *et al.* \(2000b\)](#) demonstrated correlations between $\delta^{18}\text{O}$ and other indicators of heterogeneous sources in MORB and proposed that the variations in oxygen-isotope composition reflect varying influence of recycled materials.

[Bebout and Kump \(2005\)](#) considered how the bulk isotopic composition of subducting carbon (sedimentary oxidized and reduced carbon, carbonate in AOC), the carbon inputs and outputs for arcs and whole-mantle, and the effects of varying extents of deep carbon subduction (i.e., retention during metamorphism) influence the mantle carbon budget ([Figure 22](#)). Metamorphic modifications of endmembers could have significant consequences for this mass balance (e.g., estimating proportions of inputs from sediments, AOC, mantle wedge, deeper mantle). The common occurrence of marble in UHP suites ([Becker and Altherr, 1992](#); [Zhang and Liou, 1996](#); [Reinecke, 1998](#); [Ogasawara *et al.*, 2000](#); [Zhang *et al.*, 2003](#); [Ohta *et al.*, 2003](#)), with oxygen- and carbon- isotope

compositions resembling those of seafloor carbonate, is evidence for the preservation of relatively pure carbonate lithologies to well beyond 100 km depths. Such preservation is predicted by models of decarbonation, depending on the extents of infiltration by H_2O -rich fluids capable of driving decarbonation reactions ([Kerrick and Connolly, 2001](#); [Gorman *et al.*, 2006](#)). Data for higher-grade lithologies containing both oxidized (carbonate) and reduced (graphite) carbon indicate significant carbon-isotope exchange of the two reservoirs during heating. The related evolution in carbon-isotope compositions of the two reservoirs, together with loss of carbon during devolatilization, could affect the carbon-isotope mass balance for reduced-oxidized carbon entering the deep mantle (see [Agrinier *et al.*, 1985](#)). Diamonds provide a possible, but highly convoluted, record of long-term cycling of carbon (and nitrogen) into the deep mantle (see [Cartigny, 2005](#)) and there has been considerable debate regarding the extent to which diamond carbon- (and nitrogen-) isotope compositions in some cases reflect the subduction of organic signatures (see [Deines, 2002](#)).

The U/Th/Pb system (also see [Chapter 3.15](#); [Hart and Staudigel, 1989](#); [Elliott *et al.*, 1999](#)), and its possible disruption by subduction-zone metamorphism, has been of great interest in chemical geodynamic models (see [Miller *et al.*, 1994](#); [Brenan *et al.*, 1995a](#); [Bach *et al.*, 2003](#); [Kelley *et al.*, 2005](#); see [Chapter 2.11](#) for discussion of uranium-series isotope constraints on element transport out of the downgoing plate). [Keppler \(1996\)](#) demonstrated that Pb partitions more strongly into alkali-chloride aqueous fluid than thorium and uranium. [Bach *et al.* \(2003\)](#) concluded that precursors for HIMU (mantle sources characterized by high μ values, with $\mu = ({}^{238}\text{U}/{}^{204}\text{Pb})_{t=0}$; see [Chapter 2.03](#)) can be produced from AOC after 1–2 Ga, if ~ 80 – 90% lead, 40–55% rubidium, 40% strontium, and 35–40% uranium are removed during dehydration of these lithologies. [Kelley *et al.* \(2005\)](#) concluded that uranium and lead have different “depth-loss distribution” through subduction zones, with lead loss from AOC at shallower levels and more uranium loss at greater depths. [Chauvel *et al.* \(1995\)](#) suggested that subducted sulfides house the bulk of the lead and that desulfidization reactions account for the large amounts of lead addition to arcs ([Figure 2a](#)). Experiments by [Brenan *et al.* \(1995a\)](#) indicated that dehydration of basaltic rocks (at 900 °C, 2.0 GPa) can produce aqueous fluids with excess uranium relative to thorium (cf. data for hydrous fluids in [Kessel *et al.*, 2005](#)). Only a few studies of HP and UHP rocks have addressed these issues (see [Becker](#)

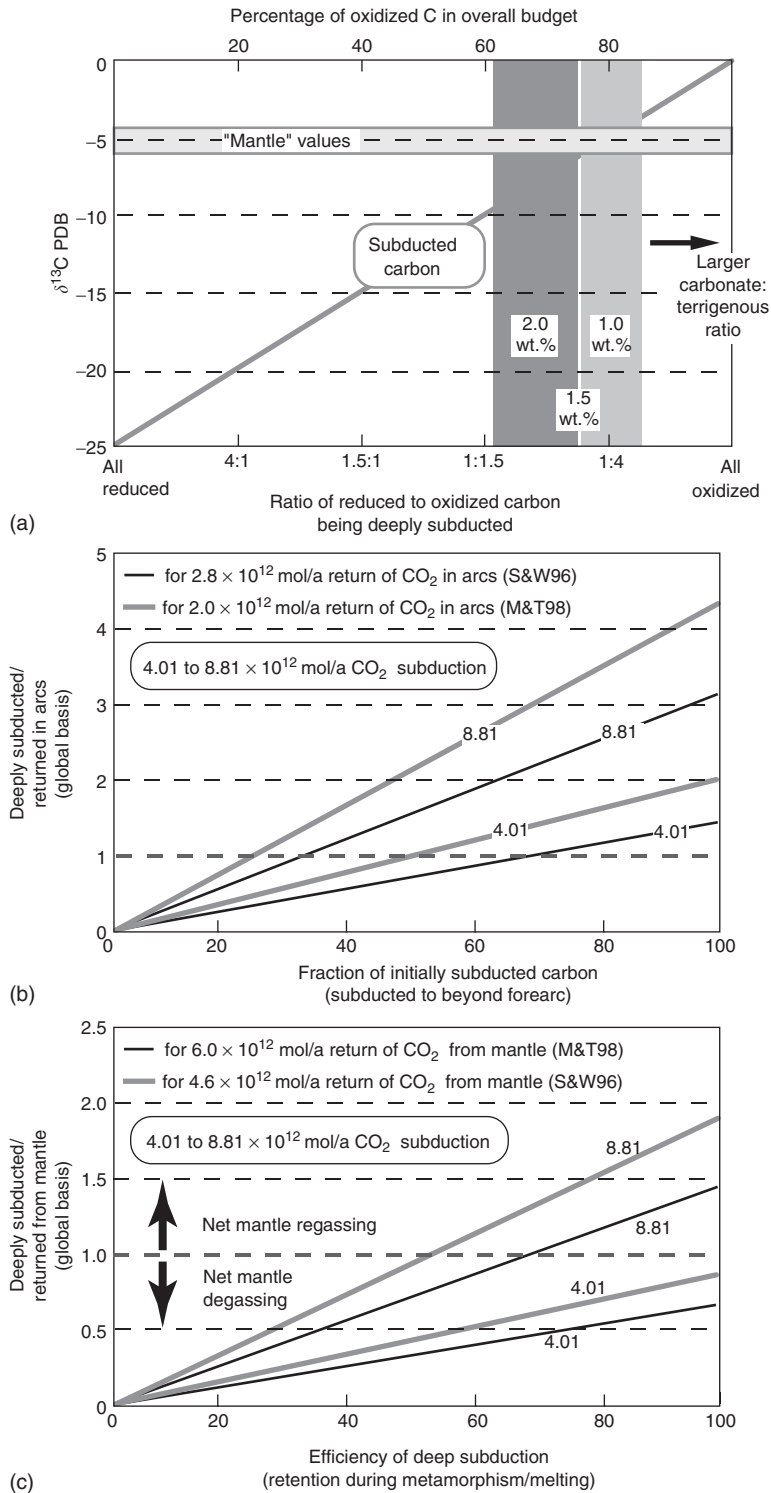


Figure 22 Carbon cycling into and out of the mantle. (a) Demonstration that, using the best estimates of modern C subduction in AOC and sediment, the canonical 1:4 ratio of reduced/oxidized C, estimated based on the mantle $\delta^{13}\text{C}$, is roughly achieved (depending on what reduced/organic C estimate is used for the "terrigenous" component in GLOSS). In (b), (c), an estimate of global C subduction in AOC and sediment is compared with two recently published estimates of C outgassing in MORB, OIB, and subduction zones (Marty and Tolstikhin, 1998; Sano and Williams, 1996). From the comparison in (a), it appears that $40 \pm 20\%$ of subducted C (here as CO_2) is returned via arc volcanic degassing. From (c), it appears that within error, the mantle could be near steady state with respect to its C budget (i.e., subduction input nearly matches output in MORB, OIB, and volcanic arcs, but with some large uncertainties). From Bebout and Kump (2005); also see Sadofsky and Bebout (2003).

et al., 2000; John *et al.*, 2004; Spandler *et al.*, 2004; Figure 8) and the results are somewhat inconclusive, pointing to a number of experiments that are needed on deeply subducted mafic and sedimentary rocks. The possible change in Th/U in HP and UHP mafic rocks, relative to either fresh or altered MORB (Figure 8d), warrants further investigation. The study of sedimentary–ultramafic metasomatic exchange by Breeding *et al.* (2004; Figure 16) seemingly demonstrates another way in which thorium, uranium, and lead could be fractionated along the slab–mantle interface.

Metamorphic disruption of the rubidium–strontium isotope system is expected in subduction zones, given that rubidium and strontium partitioning differs significantly in relevant fluid–solid systems (see Kessel *et al.*, 2005). Mahlen *et al.* (2005) suggested that Rb–Sr systematics were not disrupted by HP and UHP metamorphism of metasedimentary rocks in the Zermatt–Saas complex of the Western Alps. The Sm–Nd system should be more robust than the Rb–Sr system during metamorphism, a hypothesis that is testable by focused study of HP and UHP metamorphic suites (see Bebout, *in press*). Work on mélange formation documents robust Sm–Nd behavior in even highly metasomatized rocks in these zones of enhanced fluid flux (King *et al.*, 2006).

Finally, the changes to the Re/Os system due to subduction zone metamorphism have been considered by Becker (2000), who analyzed samples from various Alpine suites and suggested possible Re loss relative to Os during dehydration. Like the systems discussed above, “subduction processing” is invoked to varying degrees to explain aspects of crust–mantle Re–Os mixing (see discussion by Peucker-Ehrenbrink *et al.*, 2003). Some studies present evidence for extraction of Os from the subducting slab (e.g., Brandon *et al.*, 1996; McInnes *et al.*, 1999), and work by Becker (2000) on metamorphic rocks indicated extraction of Re. However, other work indicated no significant loss of Os from the subducting slab (Becker, 2000) and that Os is not added significantly to arc rocks (Borg *et al.*, 2000; Woodland *et al.*, 2002; Chesley *et al.*, 2002). Further work directed at the HP and UHP suites is required to evaluate possible metamorphic Re and Os mobility in fluids and the possible modification of deeply subducted reservoirs.

3.20.9 SOME FINAL COMMENTS

A large number of insights regarding long-term crust–mantle mixing, continental crust

formation, and even ocean chemistry, can be gained by a better understanding of trench to deep-mantle chemical cycling. Studies of B, Li, C, and N cycling into subduction zones stand out as more broadly incorporating the full set of trench-to-subarc processes (beginning with sedimentation, diagenesis, and hydrothermal alteration on the seafloor). The reader will be struck by the relatively small number of studies presenting more comprehensive chemical datasets for HP and UHP metamorphic rocks—this field is poised to advance rapidly (see Bebout, *in press*). Further work should be partly aimed at the study of fluid and element mobility at slab–mantle interface depths corresponding to those across arcs (~100–250 km), and identification of any differences in element loss as functions of changing nature of any “fluid” emanating from these deeply subducted rocks and potentially contributing to arc magmatism. Microanalytical methods should be further applied in attempts to extract information regarding element redistribution and isotope fractionation at scales of hand specimens, particularly in cases where exhumation-related overprinting is more extreme limiting whole-rock geochemical work. Some combination of geophysical and field geochemical approaches should be aimed at evaluating the volumetric significance of mélange-like mixing zones at the slab–mantle interface at subarc depths and the geochemical impact of fluid interactions along these zones. This field will, in general benefit from a better merging of field geochemical approaches with knowledge of mineral chemistry and reactions, kinetics and disequilibrium, prograde and exhumation-related P – T paths, fluid flow and fluid–rock interactions, and experiments bearing on the physical and chemical properties of fluids at HP and UHP metamorphic conditions.

Recent geochemical work on subduction-zone chemical cycling has increasingly been integrated with experimental, theoretical, and geophysical observations (e.g., Kirby *et al.*, 1996; Hacker *et al.*, 2003a, b; Peacock *et al.*, 2005), and this approach is likely to be the most productive. Geophysical constraints are necessary to provide context and a sense of scale, as geochemical research on the complex metamorphic record can “miss the forest for the trees” if it is focused only on the small scales without appreciation of how observations at that scale fit into the larger picture. The recent MARGINS Subduction Factory and SEIZE endeavors, which focus on the Central America arc-trench system, have led to successful merging of diverse geophysical, theoretical, and geochemical observations aimed at the problem of subduction-zone energy and mass transfer.

The geochemical research conducted on the Central America margin demonstrates the need to consider mass balance on an individual convergent margin basis, and the hazards of using global estimates of the geochemistry of subducting lithologies known to show great variation on the seafloor and among individual margins. In this type of approach, insights gained through study of paleosubduction suites (e.g., degrees to which elements are retained or lost during HP to UHP metamorphism) can be used to help reconcile estimated subduction inputs and outputs.

ACKNOWLEDGMENTS

I would like to acknowledge recent collaborations with, and support from E. Nakamura, T. Moriguti, and K. Kobayashi (and other colleagues at the Institute for Study of the Earth's Interior, Misasa, Mark Barton, Marty Grove, Japan). Thanks also go to my other recent collaborators, Robbie King, Long Li, Seth Sadofsky, Mark Barton, Marty Grove, Jeff Ryan, Bill Leeman, Marilyn Fogel, Ann Bebout, Philippe Agard, Bas van der Klauw, Colin Graham, and Lee Kump. Finally, I would like to thank Roberta Rudnick for her assistance (and patience) as the editor for this manuscript and John Ayers and Roberta Rudnick for their very useful and constructive reviews.

REFERENCES

- Abers G. A. (2000) Hydrated subducted crust at 100–250 km depth. *Earth Planet. Sci. Lett.* **176**, 323–330.
- Agard P., Monie P., Jolivet L., and Goffé B. (2002) Exhumation of the Schistes Lustrés complex: *in situ* laser probe $^{40}\text{Ar}/^{39}\text{Ar}$ constraints and implications for the Western Alps. *J. Meta. Geol.* **20**, 599–618.
- Agrinier P., Javoy M., Smith D. C., and Pineau F. (1985) Carbon and oxygen isotopes in eclogites, amphibolites, veins and marbles from the Western Gneiss Region, Norway. *Chem. Geol.* **52**, 145–162.
- Ague J. J. Models of permeability contrasts in subduction zone melange: implications for gradients in fluid fluxes, Syros and Tinos Islands, Greece. *Chem. Geol.* (in press).
- Allègre C. J. (1989) Mantle cycling: process and time scales. In *Crust/Mantle Recycling at Convergence Zones* (eds. S. R. Hart and L. Gulen). NATO (N. Atlantic Treaty Org.), ASI (Adv. Stud. Inst.) Ser. Kluwer, Dordrecht, pp. 1–14.
- Alt J. C. and Teagle D. A. H. (2003) Hydrothermal alteration of upper oceanic crust formed at a fast-spreading ridge: mineral, chemical, and isotopic evidence from ODP Site 801. *Chem. Geol.* **201**, 191–211.
- Altherr R., Topuz G., Marschall H., Zack T., and Ludwig T. (2004) Evolution of a tourmaline-bearing lawsonite eclogite from the Elekdag area (Central Pontides, N Turkey): evidence for infiltration of slab-derived B-rich fluids during exhumation. *Contrib. Mineral. Petrol.* **148**, 409–425.
- Arculus R. J., Lapiere H., and Jaillard E. (1999) Geochemical window into subduction and accretion processes: Raspas metamorphic complex, Ecuador. *Geology* **27**, 547–550.
- Ayers J. C. and Watson E. B. (1991) Solubility of apatite, monazite, zircon, and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry. *Phil. Trans. Roy. Soc. Lond.* **335**, 365–375.
- Bach B., Peucker-Ehrenbrink B., Hart S. R., and Blusztajn J. S. (2003) Geochemistry of hydrothermally altered oceanic crust: DSDP/ODP Hole 504B—implications for seawater-crust exchange budgets and Sr- and Pb-isotopic evolution of the mantle. *Geochem. Geophys. Geosyst.* **4**, 8904, doi:10.1029/2002GC000419.
- Barnicoat A. C. (1988) Zoned high-pressure assemblages in pillow lavas of the Zermatt-Saas ophiolite zone, Switzerland. *Lithos* **21**, 227–236.
- Barnicoat A. C. and Cartwright I. (1995) Focused fluid flow during subduction: oxygen isotope data from high-pressure ophiolites of the Western Alps. *Earth Planet. Sci. Lett.* **132**, 53–61.
- Barth M. G., Rudnick R. L., Horn I., McDonough W. F., Spicuzza M. J., Valley J. W., and Haggerty S. E. (2001) Geochemistry of xenolithic eclogites from West Africa. Part I: A link between low MgO eclogites and Archean crust formation. *Geochim. Cosmochim. Acta* **65**, 1499–1527.
- Bebout G. E. (1989) Geological and geochemical investigations of fluid flow and mass transfer during subduction-zone metamorphism. PhD Dissertation, University of California, Los Angeles, CA, 370pp.
- Bebout G. E. (1991a) Field-based evidence for devolatilization in subduction zones: implications for arc magmatism. *Science* **251**, 413–416.
- Bebout G. E. (1991b) Geometry and mechanisms of fluid flow at 15 to 45 kilometer depths of an early Cretaceous accretionary complex. *Geophys. Res. Lett.* **18**, 923–926.
- Bebout G. E. (1995) The impact of subduction-zone metamorphism on mantle-ocean chemical cycling. *Chem. Geol.* **126**, 191–218.
- Bebout G. E. (1997) Nitrogen isotope tracers of high-temperature fluid–rock interactions: case study of the Catalina Schist, California. *Earth Planet. Sci. Lett.* **151**, 77–91.
- Bebout G. E. Metamorphic chemical geodynamics of subduction zones. *Earth Planet. Sci. Lett.* (in press).
- Bebout G. E., Agard P., King R., and Nakamura E. (2004) *Record of forearc devolatilization in the Schistes Lustrés HP–UHP metasedimentary unit Western Alps (Extended Abstract)*. Proceedings of the Eleventh Water-Rock Symposium, Saratoga Springs, June/July.
- Bebout G. E. and Barton M. D. (1989) Fluid flow and metasomatism in a subduction zone hydrothermal system: Catalina Schist Terrane, California. *Geology* **17**, 976–980.
- Bebout G. E. and Barton M. D. (1993) Metasomatism during subduction: products and possible paths in the Catalina Schist, California. *Chem. Geol.* **108**, 61–92.
- Bebout G. E. and Barton M. D. (2002) Tectonic and metasomatic mixing in a high-T, subduction-zone melange—insights into the geochemical evolution of the slab–mantle interface. *Chem. Geol.* **187**, 79–106.
- Bebout G. E., Bebout A. E., and Graham C. M. Cycling of B, Li, and LILE (K, Cs, Rb, Ba, Sr) into subduction zones: SIMS evidence from micas in high-P/T metasedimentary rocks. *Chem. Geol.* (in press).
- Bebout G. E. and Fogel M. L. (1992) Nitrogen-isotope compositions of metasedimentary rocks in the Catalina Schist, California: implications for metamorphic devolatilization history. *Geochim. Cosmochim. Acta* **56**, 2139–2149.
- Bebout G. E. and Kump L. R. (2005) *Sensitivity of global carbon cycling models to changing subduction fluxes.*

- Proceedings of the Goldschmidt Conference, Moscow, Idaho.
- Bebout G. E. and Nakamura E. (2003) Record in metamorphic tourmalines of subduction-zone devolatilization and boron cycling. *Geology* **31**, 407–410.
- Bebout G. E., Ryan J. G., and Leeman W. P. (1993) B–Be systematics in subduction-related metamorphic rocks: characterization of the subducted component. *Geochim. Cosmochim. Acta* **57**, 2227–2237.
- Bebout G. E., Ryan J. G., Leeman W. P., and Bebout A. E. (1999) Fractionation of trace elements during subduction-zone metamorphism: impact of convergent margin thermal evolution. *Earth Planet. Sci. Lett.* **171**, 63–81.
- Becker H. (2000) Re–Os fractionation in eclogites and blueschists and the implications for recycling of oceanic crust into the mantle. *Earth Planet. Sci. Lett.* **177**, 2300–2387.
- Becker H. and Altherr R. (1992) Evidence from ultra-high pressure marbles for recycling of sediments into the mantle. *Nature* **358**, 745–748.
- Becker H., Carlson R. W., and Jochum K. P. (2000) Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones. *Chem. Geol.* **163**, 65–99.
- Becker H., Jochum K. P., and Carlson R. W. (1999) Constraints from high-pressure veins in eclogites on the composition of hydrous fluids in subduction zones. *Chem. Geol.* **160**, 291–308.
- Ben Othman D., White W. M., and Patchett J. (1989) The geochemistry of marine sediments, island arc magma genesis, and crust-mantle recycling. *Earth Planet. Sci. Lett.* **94**, 1–21.
- Benton L. D., Ryan J. G., and Savov I. P. (2004) Lithium abundance and isotope systematics of forearc serpentinites, Conical Seamount, Mariana forearc: insights into the mechanics of slab–mantle exchange during subduction. *Geochem. Geophys. Geosyst.* **5**(8), Q08J12, doi:10.1029/2004GC000708.
- Benton L. D., Ryan J. G., and Tera F. (2001) Boron isotope systematics of slab fluids as inferred from a serpentinite seamount, Mariana forearc. *Earth Planet. Sci. Lett.* **187**, 273–282.
- Berner R. A. (1999) A new look at the long-term carbon cycle. *GSA Today* **9**, 1–6.
- Beysac O., Rouzaud J.-N., Goffe B., Brunet F., and Chopin C. (2002) Graphitization in a high-pressure, low-temperature metamorphic gradient: a Raman microspectroscopy and HRTEM study. *Contrib. Mineral. Petrol.* **143**, 19–31, doi:10.1007/s00410-001-0324-7.
- Bindeman I. N., Eiler J. M., Yogodzinski G. M., Tatsumi Y., Stern C. R., Grove T. L., Portnyagin M., Hoernle K., and Danyushevsky L. V. (2005) Oxygen isotope evidence for slab melting in modern and ancient subduction zones. *Earth Planet. Sci. Lett.* **235**, 480–496.
- Blake M. C., Jayko A. S., McLaughlin R. J., and Underwood M. B. (1987) Metamorphic and tectonic evolution of the Franciscan Complex, Northern California. In *Metamorphism and Crustal Evolution of the Western United States*, Rubey (ed. W. G. Ernst), Prentice-Hall, Englewood Cliffs, NJ, vol. 7, pp. 1035–1060.
- Borg L. E., Brandon A. D., Clyne M. A., and Walker R. J. (2000) Re–Os isotopic systematics of primitive lavas from the Lassen region of the Cascade arc, California. *Earth Planet. Sci. Lett.* **177**, 301–317.
- Brandon A. D., Creaser R. A., Shirey S. B., and Carlson R. W. (1996) Osmium recycling in subduction zones. *Science* **272**, 861–864.
- Breeding C. M. and Ague J. J. (2002) Slab-derived fluids and quartz-vein formation in an accretionary prism, Otago Schist, New Zealand. *Geology* **30**, 499–502.
- Breeding C. M., Ague J. J., and Brocker M. (2004) Fluid–metasedimentary interactions in subduction zone mélange: implications for the chemical composition of arc magmas. *Geology* **32**, 1041–1044.
- Brenan J. M., Ryerson F. J., and Shaw H. F. (1998) The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction; experiments and models. *Geochim. Cosmochim. Acta* **62**, 3337–3347.
- Brenan J. M., Shaw H. F., Phinney D. L., and Ryerson F. J. (1994) Rutile-aqueous fluid partitioning of Nb, Ta, Hf, Zr, U, and Th: implications for high field strength element depletions in island-arc basalts. *Earth Planet. Sci. Lett.* **128**, 327–339.
- Brenan J. M., Shaw H. F., and Ryerson F. J. (1995a) Experimental evidence for the origin of lead enrichment in convergent margin magmas. *Nature* **378**, 54–56.
- Brenan J. M., Shaw H. F., Ryerson F. J., and Phinney D. L. (1995b) Mineral-aqueous fluid partitioning of trace elements at 900 °C and 2.0 GPa: constraints on the trace element geochemistry of mantle and deep crustal fluids. *Geochim. Cosmochim. Acta* **59**, 3331–3350.
- Brown K. M., Saffer D. M., and Bekins B. A. (2001) Smectite diagenesis, pore-water freshening, and fluid flow at the toe of the Nankai wedge. *Earth Planet. Sci. Lett.* **194**, 97–109.
- Brunsmann A., Franz G., and Erzinger J. (2001) REE mobilization during small-scale high-pressure fluid–rock interaction and zoisite/fluid partitioning of La to Eu. *Geochim. Cosmochim. Acta* **65**, 559–570.
- Brunsmann A., Franz G., Erzinger J., and Landwehr D. (2000) Zoisite- and clinozoisite-segregations in metabasites (Tauern Window, Austria) as evidence for high-pressure fluid–rock interaction. *J. Meta. Geol.* **18**, 1–21.
- Busigny V., Cartigny P., Philippot P., Ader M., and Javoy M. (2003) Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (Western Alps, Europe). *Earth Planet. Sci. Lett.* **215**, 27–42.
- Carr M. J., Feigenson M. D., Patino L. C., and Walker, J. A. (2003) Volcanism and geochemistry in Central America: progress and problems. In *Inside the Subduction Factory* (ed. J. Eiler), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 138, pp. 153–174.
- Cartigny P. (2005) Stable isotopes and the origin of diamond. *Elements* **1**, 79–84.
- Cartwright I. and Barnicoat A. C. (1999) Stable isotope geochemistry of Alpine ophiolites: a window to ocean-floor hydrothermal alteration and constraints on fluid–rock interaction during high-pressure metamorphism. *Int. J. Earth Sci.* **88**, 219–235.
- Chalot-Prat F. (2005) An undeformed ophiolite in the Alps: field and geochemical evidence for a link between volcanism and shallow plate processes. In *Plates, Plumes, and Paradigms* (eds. G. R. Natland, D. C. Presnall, and D. L. Anderson). *Geol. Soc. Am. Spec. Pap.* **388**, 751–780.
- Chalot-Prat F., Ganne J., and Lombard A. (2003) No significant element transfer from the oceanic plate to the mantle wedge during subduction and exhumation of the Tethys lithosphere (Western Alps). *Lithos* **69**, 69–103.
- Chauvel C., Goldstein S. L., and Hofmann A. W. (1995) Hydration and dehydration of oceanic crust controls Pb evolution in the mantle. *Chem. Geol.* **126**, 65–75.
- Chesley J., Ruiz J., Righter K., Ferrari L., and Gomez-Tuena A. (2002) Source contamination versus assimilation: an example from the Trans-Mexican Volcanic Arc. *Earth Planet. Sci. Lett.* **195**, 211–221.
- Cloos M. (1986) Blueschists in the Franciscan Complex of California: prototectonic constraints on uplift

- mechanisms. In *Blueschists and Eclogites* (eds. B. W. Evans and E. H. Brown). Geol. Soc. Am. Mem, vol. 164, pp. 77–93.
- Cloos M. (1993) Lithospheric buoyancy and collisional orogenesis; subduction of oceanic plateaus, continental margins, island arcs, spreading ridges, and seamounts. *Geol. Soc. Am. Bull.* **105**, 715–737.
- Compton J. S., Williams L. B., and Ferrell R. E., Jr. (1992) Mineralization of organogenic ammonium in the Monterey Formation, Santa Maria and San Joaquin basins, California, USA. *Geochim. Cosmochim. Acta* **56**, 1979–1991.
- Deines P. (2002) The carbon isotope geochemistry of mantle xenoliths. *Earth-Sci. Rev.* **58**, 247–278.
- Deville E., Fudral S., Lagabrielle Y., Marthaler M., and Sartori M. (1992) From oceanic closure to continental collision; a synthesis of the “Schistes Lustres” metamorphic complex of the Western Alps. *Geol. Soc. Am. Bull.* **104**, 127–139.
- Dixon J. E. and Ridley J. R. (1987) Syros. In *Chemical Transport in Metasomatic Processes* (ed. H. C. Helgeson). Reidel, Boston, pp. 489–501.
- Domanik K. J., Hervig R. L., and Peacock S. M. (1993) Beryllium and boron in subduction zone minerals: an ion microprobe study. *Geochim. Cosmochim. Acta* **57**, 4997–5010.
- Domanik K. J. and Holloway J. R. (1996) The stability and composition of phengitic muscovite and associated phases from 5.5–11 GPa; implications for deeply subducted sediments. *Geochim. Cosmochim. Acta* **60**, 4133–4150.
- Dumitru T. A. (1991) Effects of subduction parameters on geothermal gradients in forearcs, with an application to Franciscan subduction in California. *J. Geophys. Res.* **96**(B2), 621–641.
- Eiler J. M., Carr M. J., Reagan M., and Stolper E. (2005) Oxygen isotope constraints on the sources of Central American arc lavas. *Geochem. Geophys. Geosyst.* **6**, Q07007, doi:10.1029/2004GC000804.
- Eiler J., Crawford A., Elliott T., Farley K. A., Valley J. V., and Stolper E. M. (2000a) Oxygen isotope geochemistry of oceanic arc lavas. *J. Petrol.* **41**, 229–256.
- Eiler J., Schiano P., Kitchen N., and Stolper E. M. (2000b) Oxygen-isotope evidence for recycled crust in the sources of mid-ocean-ridge basalts. *Nature* **403**, 530–534.
- Elderfield H., Kastner M., and Martin J. B. (1990) Compositions and sources of fluids in sediments of the Peru subduction zone. *J. Geophys. Res.* **95**, 8819–8827.
- Elliott T. (2003) Tracers of the slab. In *Inside the Subduction Factory* (ed. J. Eiler), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 138, pp. 23–45.
- Elliott T., Jeffcoate A., and Bouman C. (2004) The terrestrial Li isotope cycle: light-weight constraints on mantle convection. *Earth Planet. Sci. Lett.* **220**, 231–245.
- Elliott T., Zindler A., and Bourdon B. (1999) Exploring the kappa conundrum: the role of recycling in the lead isotope evolution of the mantle. *Earth Planet. Sci. Lett.* **169**, 129–145.
- El-Shazly A. K. and Liou J. G. (1991) Glaucophane chloritoid-bearing assemblages from NE Oman: petrologic significance and a petrogenetic grid for high P metapelites. *Contrib. Mineral. Petrol.* **107**, 180–201.
- El-Shazly A. K. and Sisson V. B. (1999) Retrograde evolution of eclogite facies rocks from NE Oman: evidence from fluid inclusions and petrological data. *Chem. Geol.* **154**, 193–223.
- Feineman M. D., Ryerson F. J., DePaolo D. J., and Plank T. Zoisite-aqueous fluid trace element partitioning and the affect of temperature on slab-derived fluid composition. *Chem. Geol.* (in press).
- Fischer T. P., Hilton D. R., Zimmer M. M., Shaw A. M., Sharp Z. D., and Walker J. A. (2002) Subduction and recycling of nitrogen along the Central American Margin. *Science* **297**, 1154–1157.
- Fisher D. M. (1996) Fabrics and veins in the forearc: a record of cyclic fluid flow at depths of <15 km. In *Subduction: Top to Bottom* (eds. G. E. Bebout, D. W. Scholl, S. H. Kirby, and J. P. Platt), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 96, pp. 75–89.
- Fitzherbert J. A., Clarke G. L., and Powell R. (2005) Preferential retrogression of high-P metasediments and the preservation of blueschist to eclogite facies metabasite during exhumation, Diahot terrane, NE New Caledonia. *Lithos* **83**, 67–96.
- Foley S. F., Buhre S., and Jacob D. E. (2003) Evolution of the Archaean crust by delamination and shallow subduction. *Nature* **421**, 249–252.
- Franz L., Romer R. L., Klemd R., Schmid R., Oberhansli R., Wagner T., and Shuwen D. (2001) Eclogite-facies quartz veins within metabasites of the Dabie Shan (eastern China): pressure–temperature–time–deformation path, composition of the fluid phase and fluid flow during exhumation of high-pressure rocks. *Contrib. Mineral. Petrol.* **141**, 322–346.
- Frey M. (1987) Very low-grade metamorphism of clastic sedimentary rocks. In *Low Temperature Metamorphism*. Blackie Acad, New York, pp. 9–58.
- Fruh-Green G. L., Scambelluri M., and Vallis F. (2001) O–H isotope ratios of high pressure ultramafic rocks: implications for fluid sources and mobility in the subducted hydrous mantle. *Contrib. Mineral. Petrol.* **141**, 145–159.
- Fu B., Zheng Y.-F., and Touret J. L. R. (2002) Petrological, isotopic and fluid inclusion studies of eclogites from Sujiahe, NW Dabie Shan (China). *Chem. Geol.* **187**, 107–128.
- Gao J. and Klemd R. (2001) Primary fluids entrapped at blueschist to eclogite transition: evidence from the Tianshan meta-subduction complex in northwestern China. *Contrib. Mineral. Petrol.* **142**, 1–14.
- George R., Turner S., Morris J., Plank T., Hawkesworth C., and Ryan J. (2005) Pressure–temperature–time paths of sediment recycling beneath the Tonga-Kermadec arc. *Earth Planet. Sci. Lett.* **233**, 195–211.
- Getty S. R. and Selverstone J. (1994) Stable isotopic and trace element evidence for restricted fluid migration in 2 GPa eclogites. *J. Meta. Geol.* **12**, 747–760.
- Gieskes J., Blanc G., Vrolijk P., Moore J. C., Mascle A., Taylor E., Andrieff P., Alvarez F., Barnes R., Beck C., Behrmann J., Brown K., Clark M., Dolan J., Fisher A., Hounslow M. W., McLellan P., Moran K., Ogawa Y., Sakai T., Schoonmaker J., Wilkins R., and Williams C. (1989) Hydrogeochemistry in the Barbados accretionary complex: Leg 110 ODP. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **71**, 83–96.
- Gill J. B. (1981) *Orogenic Andesites and Plate Tectonics*. Springer, Berlin, 390pp.
- Giorgetti G., Tropper P., Essene E. J., and Peacor D. R. (2000) Characterization of non-equilibrium and equilibrium occurrences of paragonite/muscovite intergrowths in an eclogite from the Sesia-Lanzo Zone (Western Alps, Italy). *Contrib. Mineral. Petrol.* **138**, 326–336.
- Glodny J., Austrheim H., Molina J. F., Rusin A. I., and Seward D. (2003) Rb/Sr record of fluid–rock interaction in eclogites: the Marun-Keu complex, Polar Urals, Russia. *Geochim. Cosmochim. Acta* **67**, 4353–4371.
- Godon A., Jendrzewski N., Castrec-Rouelle D. A., Pineau F., Boulegue J., and Javoy M. (2004) Origin and evolution of fluids from mud volcanoes in the Barbados accretionary complex. *Geochim. Cosmochim. Acta* **68**, 2153–2165.

- Gorman P. J., Kerrick D. M., and Connolly J. A. D. (2006) Modeling open system metamorphic decarbonation of subducting slabs. *Geochem. Geophys. Geosyst.* **7**, Q04007, doi:10.1029/2005GC001125.
- Gray D. R., Gregory R. T., and Durney D. W. (1991) Rock-buffered fluid–rock interaction in deformed quartz-rich turbidite sequences eastern Australia. *J. Geophys. Res.* **93**, 4625–4656.
- Green T. H. and Adam J. (2003) Experimentally determined trace element characteristics of aqueous fluid from dehydrated mafic oceanic crust at 3.0 GPa, 650–750 °C. *Eur. J. Mineral.* **15**, 815–830.
- Gregory R. T. and Taylor H. P. (1981) An oxygen isotope profile in a section of Cretaceous oceanic-crust, Samail Ophiolite, Oman—evidence for delta-18-O buffering of the oceans by deep (less-than 5 km) seawater-hydrothermal circulation at mid-ocean ridges. *J. Geophys. Res.* **86**(B4), 2737–2755.
- Grove M. and Bebout G. E. (1995) Cretaceous tectonic evolution of coastal southern California: insights from the Catalina Schist. *Tectonics* **14**, 1290–1308.
- Hacker B. R. Pressures and temperatures of ultra-high-pressure metamorphism: implications for UHP tectonics and H₂O in subducting slabs. *Int. Geol. Rev.* (in press).
- Hacker B. R., Abers G. A., and Peacock S. M. (2003a) Subduction factory. 1: Theoretical mineralogy, densities, seismic wave speeds, and H₂O contents. *J. Geophys. Res.* **108**(B1), 2029, doi:10.1029/2001JB001127.
- Hacker B. R., Luffi P., Lutkov V., Minaev V., Ratschbacher L., Plank T., Ducea M., Patino-Douce A., McWilliams M., and Metcalf J. (2005) Near-ultrahigh pressure processing of continental crust: Miocene crustal xenoliths from the Pamir. *J. Petrol.* **46**, 1661–1687.
- Hacker B. R., Peacock S. M., Abers G. A., and Holloway S. D. (2003b) Subduction factory. 2: Are intermediate-depth earthquakes in subducting slabs linked to metamorphic dehydration reactions. *J. Geophys. Res.* **108**(B1), 2030, doi:10.1029/2001JB001129.
- Hart S. R. and Reid M. R. (1991) Rb/Cs fractionation: a link between granulite metamorphism and the S-process. *Geochim. Cosmochim. Acta* **55**, 2379–2382.
- Hart S. R. and Staudigel H. (1989) Isotopic characterization and identification of recycled components. In *Crust/Mantle Recycling at Convergence Zones* (eds. S. R. Hart and L. Gulen). NATO (N. Atlantic Treaty Org.), ASI (Adv. Stud. Inst.) Ser. Kluwer, Dordrecht, pp. 15–28.
- Hattori K. H. and Guillot S. (2003) Volcanic fronts form as a consequence of serpentinite dehydration in the forearc mantle wedge. *Geology* **31**, 525–528.
- Henry C., Burkhard M., and Goffe B. (1996) Evolution of synmetamorphic veins and their wallrocks through a Western Alps transect: no evidence for large-scale fluid flow. Stable isotope, major- and trace-element systematics. *Chem. Geol.* **127**, 81–109.
- Hermann J., Spandler C., Hack A., and Korsakov A. V. Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: implications for element transfer in subduction zones. *Lithos.* (in press).
- Hilton D. R., Fischer T. P., and Marty, B. (2002) Noble gases and volatile recycling at subduction zones. In *Noble Gases in Geochemistry and Cosmochemistry* (eds. D. Porcelli, C. J. Ballentine, and R. Wieler). *Rev. Mineral. Geochem.*, Mineralogical Society of America and Geochemical Society, Washington, DC vol. 47, pp. 319–370.
- Hofmann A. W. (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.* **90**, 297–314.
- Ishikawa T. and Nakamura E. (1994) Origin of the slab component in arc lavas from across-arc variation of B and Pb isotopes. *Nature* **370**, 205–208.
- Ishikawa T. and Tera F. (1997) Source, composition and distribution of the fluid in the Kurile mantle wedge: constraints from across-arc variations of B/Nb and B isotopes. *Earth Planet. Sci. Lett.* **152**, 123–138.
- Ito E., Harris D. M., and Anderson A. T., Jr. (1983) Alteration of oceanic crust and geologic cycling of chlorite and water. *Geochim. Cosmochim. Acta* **47**, 1613–1624.
- Jahn B. M. (1999) Sm–Nd isotope tracer study of UHP metamorphic rocks: implications for continental subduction and collisional tectonics. *Int. Geol. Rev.* **41**, 859–885.
- Jarrard R. D. (2003) Subduction fluxes of water, carbon dioxide, chlorine, and potassium. *Geochem. Geophys. Geosyst.* **5**, doi:10.1029/2002GC000392.
- Javoy M. (1998) The birth of the Earth's atmosphere: the behaviour and fate of its major elements. *Chem. Geol.* **147**, 11–25.
- John T. and Schenk V. (2003) Partial eclogitisation of gabbroic rocks in a late Precambrian subduction zone (Zambia): prograde metamorphism triggered by fluid infiltration. *Contrib. Mineral. Petrol.* **146**, 174–191, doi:10.1007/s00410-003-0492-8.
- John T., Scherer E. E., Haase K., and Schenk V. (2004) Trace element fractionation during fluid-induced eclogitization in a subducting slab: trace element and Lu–Hf–Sm–Nd isotope systematics. *Earth Planet. Sci. Lett.* **227**, 441–456.
- Johnson M. C. and Plank T. (1999) Dehydration and melting experiments constrain the fate of subducted sediments. *Geochem. Geophys. Geosyst.* **1**, paper number 1999GC000014.
- Jolivet L., Faccena C., Goffe B., Burov E., and Agard P. (2003) Subduction tectonics and exhumation of high-pressure metamorphic rocks in the Mediterranean orogens. *Am. J. Sci.* **303**, 353–409.
- Kastner M., Elderfield H., and Martin J. B. (1991) Fluids in convergent margins: what do we know about their composition, origin, role in diagenesis and importance for oceanic chemical fluxes? *Philos. Trans. Roy. Soc. Lond.* **335**, 243–259.
- Kelemen P. B., Rilling J. L., Parmentier E. M., Mehl L., and Hacker B. R. (2003) Thermal structure due to solid-state flow in the mantle wedge. In *Inside the Subduction Factory* (ed. J. Eiler), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 138, pp. 293–311.
- Kelley K. A., Plank T., Farr L., Ludden J., and Staudigel H. (2005) Subduction cycling of U, Th, and Pb. *Earth Planet. Sci. Lett.* **234**, 369–383.
- Kelley K. A., Plank T., Ludden J., and Staudigel H. (2003) The composition of altered oceanic crust and ODP Sites 801 and 1149. *Geochem. Geophys. Geosyst.* **4**, 8910, doi:10.1029/2002GC000435.
- Keppeler H. (1996) Constraints from partitioning experiments on the composition of subduction-zone fluids. *Nature* **380**, 237–240.
- Kerrick D. M. (2002) Serpentinite seduction. *Science* **298**, 1344–1345.
- Kerrick D. M. and Connolly J. A. D. (2001) Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature* **411**, 293–296.
- Kessel R., Schmidt M. W., Ulmer P., and Pettke T. (2005) Trace element signature of subduction-zone fluids, melts and supercritical fluids at 120–180 km depths. *Nature* **437/29**, 724–727.
- Kimura G., Silver E. A., Blum, P., et al. (1997) Proceedings of the ODP, Initial Reports, 170, College Station, TX (Ocean Drilling Program).

- King R. L. (2006) *Mélange à trois*: metamorphic controls on recycling and mass transfer within subduction zones. PhD Dissertation, Lehigh University.
- King R. L., Bebout G. E., Kobayashi K., Nakamura E., and van der Klauw S. N. G. C. (2004) Ultrahigh-pressure metabasaltic garnets as probes into deep subduction-zone chemical cycling. *Geochem. Geophys. Geosyst.* **5**(12), Q12J14, doi:10.1029/2004GC000746.
- King R. L., Bebout G. E., Moriguti T., and Nakamura E. (2006) Elemental mixing systematics and Sr–Nd isotope geochemistry of *mélange* formation: obstacles to identification of fluid sources to arc volcanics. *Earth Planet. Sci. Lett.* **246**, 288–304.
- King R. L., Kohn M. J., and Eiler J. M. (2003) Constraints on the petrologic structure of the subduction zone slab–mantle interface from the Franciscan Complex exotic ultramafic blocks. *Geol. Soc. Am. Bull.* **115**, 1097–1109.
- Kirby S., Engdahl E. R., and Denlinger, R. (1996) Intraslab earthquakes and arc volcanism: dual expressions of crustal and upper mantle metamorphism in subducting slabs. In *Subduction: Top to Bottom* (eds. G. E. Bebout, D. W. Scholl, S. H. Kirby, and J. P. Platt), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 96, pp. 195–214.
- Kullerød K., Stephens M. B., and Zachrisson E. (1990) Pillow lavas as protoliths for eclogites: evidence from a late Precambrian–Cambrian continental margin, Seve Nappes, Scandinavian Caledonides. *Contrib. Mineral. Petrol.* **105**, 1–10.
- Kurahashi E., Nakajima Y., and Ogasawara Y. (2001) Coesite inclusions and prograde compositional zonation of garnet in eclogite from Zekou in the Su-Lu ultrahigh-pressure terrane, eastern China. *J. Mineral. Petrol. Sci.* **96**, 100–108.
- Kvenvolden K. A. (1993) Gas hydrates—geological perspective and global change. *Rev. Geophys.* **31**(2), 173–187.
- Lapen T. J., Johnson C. M., Baumgartner L. P., Mahlen N. J., Beard B. L., and Amato J. M. (2003) Burial rates during prograde metamorphism of an ultrahigh-pressure terrane: an example from Lago di Cignana, Western Alps, Italy. *Earth Planet. Sci. Lett.* **215**, 57–72.
- Laurora A., Mazzucchelli M., Rivalenti G., Vannucci R., Zanetti A., Barbieri M. A., and Cingolani C. A. (2001) Metasomatism and melting in carbonated peridotite xenoliths from the mantle wedge: the Gobernador Gregores case (Southern Patagonia). *J. Petrol.* **42**, 69–87.
- Leeman W. P. (1996) Boron and other fluid-mobile element systematics in volcanic arc lavas: implications for subduction processes. In *Subduction: Top to Bottom* (eds. G. E. Bebout, D. W. Scholl, S. H. Kirby, and J. P. Platt), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 96, pp. 269–276.
- Li L. and Bebout G. E. (2005) Carbon and nitrogen geochemistry of sediments in the Central American convergent margin: insights regarding paleoproductivity and carbon and nitrogen subduction fluxes. *J. Geophys. Res.* **110**, B11202, doi:10.1029/2004JB003276.
- Li S., Jagoutz E., Chen Y., and Li Q. (2000) Sm–Nd and Rb–Sr isotopic chronology and cooling history of ultrahigh pressure rocks and their country rocks at Shuanghe in the Dabie Mountains, Central China. *Geochim. Cosmochim. Acta* **64**, 1077–1093.
- Liou J. G., Maruyama S., and Cho M. (1987) Very low-grade metamorphism of volcanic and volcanoclastic rocks—mineral assemblages and mineral facies. In *Low Temperature Metamorphism* (ed. M. Frey). Blackie Academy, New York, pp. 59–113.
- MacPherson G. J., Phipps S. P., and Grossman J. N. (1990) Diverse sources for igneous blocks in Franciscan mélanges, California Coast Ranges. *J. Geol.* **98**, 845–862.
- Maekawa H., Shozui M., Ishii T., Fryer P., and Pearce J. A. (1993) Blueschist metamorphism in an active subduction zone. *Nature* **364**, 520–523.
- Magaritz M. and Taylor H. (1976) Oxygen, hydrogen and carbon isotope studies of the Franciscan formation, Coast Ranges, California. *Geochim. Cosmochim. Acta.* **40**, 215–234.
- Magna T., Wiechert U., Grove T. L., and Halliday A. N. Lithium isotope fractionation in the southern Cascadia subduction zone. *Earth Planet. Sci. Lett.* (in press).
- Mahlen N. J., Johnson C. M., Baumgartner L. P., and Beard B. L. (2005) Provenance of Jurassic Tethyan sediments in the HP/UHP Zermatt-Saas ophiolite, Western Alps. *Geol. Soc. Am.* **117**, 530–544.
- Manning C. E. (1998) Fluid composition at the blueschist–eclogite transition in the model system Na₂O–MgO–Al₂O₃–SiO₂–H₂O–HCl, Schweiz. *Mineral. Petrogr. Mitt.* **78**, 225–242.
- Manning C. E. (2004) The chemistry of subduction-zone fluids. *Earth Planet. Sci. Lett.* **223**, 1–16.
- Marschall H. R., Altherr R., Ludwig T., Kalt A., Gmeling K., and Kasztovszky Z. (2006) Partitioning and budget of Li, Be, and B in high-pressure metamorphic rocks. *Geochim. Cosmochim. Acta* **70**, 4750–4769.
- Marschall H. R., Altherr R., and Rupke L. Squeezing out the slab—modeling the release of Li, Be, and B during progressive high-pressure metamorphism. *Chem. Geol.* (in press).
- Martin H. (1986) Effect of steeper Archean geothermal gradient on geochemistry of subduction-zone magmas. *Geology* **14**, 753–756.
- Marty B. and Tolstikhin I. N. (1998) CO₂ fluxes from mid-ocean ridges, arcs and plumes. *Chem. Geol.* **145**, 233–248.
- Maruyama S. and Liou J. G. (1989) Possible depth limit for underplating by a seamount. *Tectonophysics* **160**, 327–337.
- Massone H.-J. and Kopp J. (2005) A low-variance mineral assemblage with talc and phengite in an eclogite from the Saxonian Erzgebirge, Central Europe, and its P–T evolution. *J. Petrol.* **46**, 355–375.
- Maurer R. C., Defant M. J., and Joron J. L. (1992) Metasomatism of the sub-arc mantle inferred from trace elements in Philippine xenoliths. *Nature* **360**, 661–663.
- McDonough W. F. and Sun S.-S. (1995) The composition of the Earth. *Chem. Geol.* **120**, 223–253.
- McInnes G. I. A., McBride J. S., Evans N. J., Lambert D. D., and Andrew A. S. (1999) Osmium isotope constraints on ore metal recycling in subduction zones. *Science* **286**, 512–516.
- Melzer S. and Wunder B. (2001) K–Rb–Cs partitioning between phlogopite and fluid: experiments and consequences for the LILE signatures of island arc basalts. *Lithos* **59**, 69–90.
- Messiga B., Tribuzio R., Bottazzi P., and Ottolini L. (1995) An ion microprobe study on trace element composition of clinopyroxenes from blueschist and eclogitized Fe–Ti–gabbros, Ligurian Alps, northwestern Italy: some petrologic considerations. *Geochim. Cosmochim. Acta* **59**, 59–75.
- Miller D. M., Goldstein S. L., and Langmuir C. H. (1994) Cerium/lead and lead isotope ratios in arc magmas and the enrichment of lead in the continents. *Nature* **368**, 514–520.
- Miller J. A., Buick I. S., Cartwright I., and Barnicoat A. (2002) Fluid processes during the exhumation of high-P metamorphic belts. *Mineral. Mag.* **66**, 93–119.

- Molina J. F., Poli S., Austrheim H., Glodny J., and Rusin A. (2004) Eclogite-facies vein systems in the Marun–Keu complex (Polar Urals, Russia): textural, chemical and thermal constraints for patterns of fluid flow in the lower crust. *Contrib. Mineral. Petrol.* **147**, 484–504.
- Moore D. E. (1984) Metamorphic history of a high-grade blueschist exotic block from the Franciscan Complex, California. *J. Petrol.* **25**, 126–150.
- Moore G. F., Taira A., Klaus A., *et al.* (2001) New insights into deformation and fluid flow processes in the Nankai Trough accretionary prism: results of Ocean Drilling Program Leg 190. *Geochem. Geophys. Geosyst.* **2**(Oct), 2001GC0000166.
- Moore J. C. and Volijk P. (1992) Fluids in accretionary prisms. *Rev. Geophys.* **30**, 113–135.
- Moran A. E., Sisson V. B., and Leeman W. P. (1992) Boron depletion during progressive metamorphism: implications for subduction processes. *Earth Planet. Sci. Lett.* **111**, 331–349.
- Moriguti T. and Nakamura E. (1998) Across-arc variation of Li isotopes in lavas and implications for crust/mantle recycling at subduction zones. *Earth Planet. Sci. Lett.* **163**, 167–174.
- Moriguti T., Shibata T., and Nakamura E. (2004) Lithium, boron and lead isotope and trace element systematics of Quaternary basaltic volcanic rocks in northeastern Japan: mineralogical controls on slab-derived fluid composition. *Chem. Geol.* **212**, 81–100.
- Morris J. D., Valentine R., and Harrison T. (2002) ¹⁰Be imaging of sediment accretion and subduction along the northeast Japan and Costa Rica convergent margins. *Geology* **30**, 59–62.
- Mottl M. J., Wheat C. G., Fryer P., Gharib J., and Martin J. B. (2004) Chemistry of springs across the Mariana forearc shows progressive devolatilization of the subducting slab. *Geochim. Cosmochim. Acta* **68**, 4915–4933.
- Murdmaa I., Gordeev V., Kuzima T., Turanskaya N., and Mikhailov M. (1980) Geochemistry of the Japan trench sediments recovered on deep sea drilling project legs 56 and 57. *Init. Rep. DSDP*, **56–57**, 1213–1232.
- Nadeau S., Philippot P., and Pineau F. (1993) Fluid inclusion and mineral isotopic compositions (H–C–O) in eclogitic rocks as tracers of local fluid migration during high-pressure metamorphism. *Earth Planet. Sci. Lett.* **114**, 431–448.
- Nakano T. and Nakamura E. (2001) Boron isotope geochemistry of metasedimentary rocks and tourmalines in a subduction-zone metamorphic suite. *Phys. Earth Planet. Int.* **127**, 233–252.
- Nelson B. K. (1995) Fluid flow in subduction zones: evidence from Nd- and Sr-isotope variations in metabasalts of the Franciscan Complex, California. *Contrib. Mineral. Petrol.* **119**, 247–262.
- Noll P. D., Newsom H. E., Leeman W. P., and Ryan J. (1996) The role of hydrothermal fluids in the production of subduction zone magmas: evidence from siderophile and chalcophile trace elements and boron. *Geochim. Cosmochim. Acta* **60**, 587–611.
- Ogasawara Y., Ohta M., Fukasawa K., Katayama I., and Maruyama S. (2000) Diamond-bearing and diamond-free metacarbonate rocks from Kumdy-Kol and Kokchetav Massif, northern Kazakhstan. *Isl. Arc* **9**, 400–416.
- Ohta M., Mock T., Ogasawara Y., and Rumble D. (2003) Oxygen, carbon, and strontium isotope geochemistry of diamond-bearing carbonate rocks from Kumdy-Kol Kokchetav Massif, Kazakhstan. *Lithos* **70**, 77–90.
- Okamoto K. and Maruyama S. (1999) The high-pressure synthesis of lawsonite in the MORB + H₂O system. *Am. Mineral.* **84**, 362–373.
- Okamura Y. (1991) Large-scale mélange formation due to seamount subduction: an example from the Mesozoic accretionary complex in central Japan. *J. Geol.* **99**, 661–674.
- O’Leary J., Kitchen N., and Eiler J. (2002) *Hydrogen isotope geochemistry of Mariana Trough lavas (abstract)*. Fall Am. Geophys. Un., San Francisco, December, 2002.
- Paquin J., Altherr R., and Ludwig T. (2004) Li–Be–B systematics in the ultrahigh-pressure garnet peridotite from Alpe Arami (Central Swiss Alps): implications for slab-to-mantle wedge transfer. *Earth Planet. Sci. Lett.* **218**, 507–519.
- Parkinson C. D. (1996) The origin and significance of metamorphosed tectonic blocks in mélange: evidence from Sulawesi Indonesia. *Terra Nova* **8**, 312–323.
- Pawley A. R. (1994) The pressure and temperature stability limits of lawsonite: implications for H₂O recycling in subduction zones. *Contrib. Mineral. Petrol.* **118**, 99–108.
- Peacock S. M. (1992) Blueschist-facies metamorphism, shear heating, and *P–T–t* paths in subduction shear zones. *J. Geophys. Res.* **97**, 17693–17707.
- Peacock S. M. (2001) Are the lower planes of double seismic zones caused by serpentine dehydration in subducting oceanic mantle? *Geology* **29**, 299–302.
- Peacock S. M. (2003) Thermal structure and metamorphic evolution of subducting slabs. In *Inside the Subduction Factory* (ed. J. Eiler), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 138, pp. 7–22.
- Peacock S. M. and Hervig R. L. (1999) Boron isotopic composition of subduction-zone metamorphic rocks. *Chem. Geol.* **160**, 281–290.
- Peacock S. M. and Hyndman R. D. (1999) Hydrous minerals in the mantle wedge and the maximum depth of subduction zone earthquakes. *Geophys. Res. Lett.* **26**, 2517–2520.
- Peacock S. M., van Keken P. E., Holloway S. D., Hacker B. R., Abers G. A., and Ferguson R. L. (2005) Thermal structure of the Costa Rica–Nicaragua subduction zone. *Phys. Earth Planet. Int.* **149**, 187–200.
- Pearce J. A. and Peate D. W. (1995) Tectonic implications of the composition of volcanic arc magmas. *Ann. Rev. Earth Planet. Sci.* **23**, 251–285.
- Peucker-Ehrenbrink B., Bach W., Hart S. R., Blusztajn J. S., and Abbruzzese T. (2003) Rhenium–osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP Sites 504 and 417/418. *Geochem. Geophys. Geosyst.* **4**, 8911, doi: 10.1029/2002GC000414.
- Philippot P. (1993) Fluid–melt–rock interaction in mafic eclogites and coesite-bearing metasediments: constraints on volatile recycling during subduction. *Chem. Geol.* **108**, 93–112.
- Philippot P., Agrinier P., and Scambelluri M. (1998) Chlorine cycling during subduction of altered oceanic crust. *Earth Planet. Sci. Lett.* **161**, 33–44.
- Philippot P. and Selverstone J. (1991) Trace-element-rich brines in eclogitic veins: implications for fluid compositions and transport during subduction. *Contrib. Mineral. Petrol.* **106**, 417–430.
- Pickering K. T., Marsh N. G., and Dickie B. (1993) Data report: inorganic major, trace, and rare earth element analyses of the muds and mudstones from Site 808. *Init. Rep. DSDP* **131**, 427–450.
- Plank T. (2005) Constraints from thorium/lanthanum on sediment recycling at subduction zones and the evolution of the continents. *J. Petrol.* **46**, 921–944.
- Plank T. and Langmuir C. (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* **145**, 325–394.

- Plank T. and Langmuir C. H. (1993) Tracing trace elements from sediment input to volcanic output at subduction zones. *Nature* **362**, 739–743.
- Plank T. and Ludden J. (1992) Geochemistry of sediments in the Argo Abyssal Plain at ODP Site 765: a continental margin reference section for sediment recycling in subduction zones. *Proc. ODP Sci. Res.* **123**, 167–189.
- Poli S. and Schmidt M. W. (1997) The high pressure stability of hydrous phases in orogenic belts: an experimental approach on eclogite forming processes. *Tectonophysics* **273**, 169–184.
- Poreda R. (1985) Helium-3 and deuterium in back-arc basalts: Lau Basin and the Mariana Trough. *Earth Planet. Sci. Lett.* **73**, 244–254.
- Proyer A. (2003) Metamorphism of pelites in NKFMAH—a new petrogenetic grid with implications for the preservation of high-pressure mineral assemblages during exhumation. *J. Meta. Geol.* **21**, 493–509.
- Ranero C. R., Villasenor A., Phipps Morgan J., and Weinreb W. (2005) Relationship between bend-faulting at trenches and intermediate-depth seismicity. *Geochem. Geophys. Geosyst.* **6**(12), Q12002, doi:10.1029/2005GC000997.
- Rea D. K. and Ruff L. J. (1996) Composition and mass flux of sedimentary materials entering the World's subduction zones: implications for global sediment budgets, great earthquakes, and volcanism. *Earth Planet. Sci. Lett.* **140**, 1–12.
- Reinecke T. (1998) Prograde high- to ultrahigh-pressure metamorphism and exhumation of oceanic sediments at Lago di Cignana, Zermatt-Saas Zone, Western Alps. *Lithos* **42**, 147–189.
- Ritger S., Carson B., and Suess E. (1987) Methane-derived authigenic carbonates formed by subduction-induced pore-water expulsion along the Oregon/Washington margin. *Geol. Soc. Am. Bull.* **98**, 147–156.
- Rosner M., Erzinger J., Franz G., and Trumbull R. B. (2003) Slab-derived boron isotope signatures in arc volcanic rocks from the Central Andes and evidence for boron isotope fractionation during progressive slab dehydration. *Geochem. Geophys. Geosyst.* **4**, doi:10.1029/2002GC000438.
- Rubatto D. and Hermann J. (2003) Zircon formation during fluid circulation in eclogites (Monviso, Western Alps): implications for Zr and Hf budget in subduction zones. *Geochim. Cosmochim. Acta* **67**, 2173–2187.
- Rumble D. and Yui T.-F. (1998) The Qinglongshan oxygen and hydrogen isotope anomaly near Donghai in Jiangsu Province, China. *Geochim. Cosmochim. Acta* **62**, 3307–3321.
- Rupke L. H., Morgan J. P., Hort M., and Connolly J. A. D. (2002) Are the regional differences in Central American arc lavas due to differing basaltic versus peridotitic slab sources of fluids? *Geology* **30**, 1035–1038.
- Rupke L. H., Morgan J. P., Hort M., and Connolly J. A. D. (2004) Serpentine and the subduction zone water cycle. *Earth Planet. Sci. Lett.* **223**, 17–34.
- Ryan J., Morris J., Bebout G., Leeman B., Tera F. (1996) Describing chemical fluxes in subduction zones: insights from “depth-profiling” studies of arc and forearc rocks. In *Subduction: Top to Bottom* (eds. G. E. Bebout, D. W. Scholl, S. H. Kirby, and J. P. Platt), Am. Geophys. Un. Geophys. Monogr., vol. 96, pp. 263–268.
- Ryan J. G., Morris J. D., Tera F., Leeman W. P., and Tsvetkov A. (1995) Cross-arc geochemical variations in the Kurile island arc as a function of slab depth. *Science* **270**, 625–628.
- Sadofsky S. J. and Bebout G. E. (2003) Record of forearc devolatilization in low-T, high-P/T metasedimentary suites: significance for models of convergent margin chemical cycling. *Geochem. Geophys. Geosyst.* **4**(4).
- Sadofsky S. J. and Bebout G. E. (2004a) Nitrogen geochemistry of subducting sediments: new results from the Izu–Bonin–Mariana Margin and insights regarding global nitrogen subduction. *Geochem., Geophys. Geosyst.* **5**, Q03115, doi:10.1029/2003GC000543.
- Sadofsky S. J. and Bebout G. E. (2004b) Field and isotopic evidence for fluid mobility in the Franciscan Complex: forearc paleohydrogeology to depths of 30 km. *Int. Geol. Rev.* **46**, 1053–1088.
- Saha A., Basu A. R., Wakabayashi J., and Wortman G. L. (2005) Geochemical evidence for a subducted infant arc in Franciscan high-grade-metamorphic tectonic blocks. *Geol. Soc. Am. Bull.* **117**, 1318–1335.
- Sample J. C. and Reid M. R. (1998) Contrasting hydrogeologic regimes along strike-slip and thrust faults in the Oregon convergent margin: evidence from the chemistry of syntectonic carbonate cements and veins. *Geol. Soc. Am. Bull.* **110**, 48–59.
- Sano Y. and Williams S. N. (1996) Fluxes of mantle subducted carbon along convergent margins. *Geophys. Res. Lett.* **23**, 2749–2752.
- Sassi R., Harte B., Carswell D. A., and Yujing H. (2000) Trace element distribution in Central Dabie eclogites. *Contrib. Mineral. Petrol.* **139**, 298–315.
- Savov I. P., Ryan J. G., D'Antonio M., Kelley K., and Mattie P. (2005) Geochemistry of serpentinitized peridotites from the Mariana forearc Conical Seamount, ODP Leg 125: implications for the elemental recycling at subduction zones. *Geochem. Geophys. Geosyst.* **6**(4), Q04J15, doi:10.1029/2004GC000777.
- Scambelluri M., Fiebig J., Malaspina N., Muntener O., and Pettko T. (2004a) Serpentine subduction: implications for fluid processes and trace-element recycling. *Int. Geol. Rev.* **46**, 595–613.
- Scambelluri M., Hermann J., Morten L., and Rampone E. (2006) Melt- versus fluid-induced metasomatism in spinel to garnet wedge peridotites (Ulten Zone, Eastern Italian Alps): clues from trace element and Li abundances. *Contrib. Mineral. Petrol.* **151**, 372–394, doi:10.1007/s00410-006-0064-9.
- Scambelluri M., Muntener O., Ottolini L., Pettko T., and Vannucci R. (2004b) The fate of B, Cl, and Li in the subducted oceanic mantle and in the antigorite breakdown fluids. *Earth Planet. Sci. Lett.* **222**, 217–234.
- Scambelluri M. and Philippot P. (2001) Deep fluids in subduction zones. *Lithos* **55**, 213–227.
- Schiano P., Clocchiatti R., Shimizu N., Maury R. C., Jochum K. P., and Hofmann A. W. (1995) Hydrous, silica-rich melts in the subarc mantle and their relationships with erupted arc lavas. *Nature* **377**, 595–600.
- Scholl D. W., and von Huene R. Crustal recycling at modern subduction zones applied to the past—issues of growth and preservation of continental basement, mantle geochemistry, and supercontinent reconstruction. In *The 4D Framework of Continental Crust* (eds. R. D. Hatcher, Jr., M. P. Carlson, J. H. McBride, and J. R. Martinez Catalan), Geol. Soc. Amer. Spec. Paper. (in press).
- Sharp Z. D. and Barnes J. D. (2004) Water-soluble chlorides in mass seafloor serpentinites: a source of chloride in subduction zones. *Earth Planet. Sci. Lett.* **226**, 243–254.
- Sharp Z. D., Essene E. J., and Hunziker J. C. (1993) Stable isotope geochemistry and phase equilibria of coesite-bearing whiteschists, Dora-Maira Massif, Western Alps. *Contrib. Mineral. Petrol.* **114**, 1–12.
- Shaw A. M., Hilton D. R., Fischer T. P., Walker J. A., and Alvarado G. E. (2003) Contrasting He-C relationships in Nicaragua and Costa Rica: insights into C cycling through subduction zones. *Earth Planet. Sci. Lett.* **214**, 499–513.

- Shervais J. W., Zoglmann Schuman M. M., and Hanan B. B. (2005) The Stonyford volcanic complex: a forearc seamount in the northern California Coast Ranges. *J. Petrol.* **46**, 2091–2128.
- Skora S., Baumgartner L. P., Mahlen N. J., Johnson C. M., Pilet S., and Hellebrand E. Diffusion-limited REE uptake by eclogite garnets and its consequences for Lu–Hf and Sm–Nd geochronology. *Contrib. Mineral. Petrol.* (in press).
- Snyder G., Poreda R., Fehn U., and Hunt A. (2003) Sources of nitrogen and methane in Central American geothermal settings: noble gas and ¹²⁹I evidence for crustal and magmatic volatile components. *Geochem. Geophys., Geosyst.* **4**.
- Solomon E. A., Kastner M., and Robertson G. (2006) Barium cycling at the Costa Rica convergent margin. In: *Proceedings of the ODP, Sci. Results 205* (eds. J. M. Morris, H. W. Villinger, and A. Klaus), pp. 1–21.
- Sorensen S. S. (1991) Petrogenetic significance of zoned allanite in garnet amphibolites from a paleo-subduction zone: Catalina Schist, southern California. *Am. Mineral.* **76**, 589–601.
- Sorensen S. S. and Barton M. D. (1987) Metasomatism and partial melting in a subduction complex, Catalina Schist, southern California. *Geology* **15**, 115–118.
- Sorensen S. S. and Grossman J. N. (1989) Enrichment of trace elements in garnet amphibolites from a paleo-subduction zone: Catalina Schist, southern California. *Geochim. Cosmochim. Acta* **53**, 3155–3178.
- Sorensen S. S. and Grossman J. N. (1993) Accessory minerals and subduction zone metasomatism: a geochemical comparison of two melanges (Washington and California, USA). *Chem. Geol.* **110**, 269–297.
- Sorensen S. S., Grossman J. N., and Perfit M. R. (1997) Phengite-hosted LILE-enrichment in eclogite and related rocks: implications for fluid-mediated mass transfer in subduction zones and arc magma genesis. *J. Petrol.* **38**, 3–34.
- Spandler C. and Hermann J. (2006). High-pressure veins in eclogite from New Caledonia and their significance for fluid migration in subduction zones. *Lithos* **89**, 135–153.
- Spandler C., Hermann J., Arculus R., and Mavrogenes J. (2003) Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction processes. *Contrib. Mineral. Petrol.*, online article, **146**, 205–222, doi:10.1007/s00410-003-495-5.
- Spandler C., Hermann J., Arculus R., and Mavrogenes J. (2004) Geochemical heterogeneity and elemental mobility in deeply subducted oceanic crust; insights from high-pressure mafic rocks from New Caledonia. *Chem. Geol.* **206**, 21–42.
- Spivack A. J., Kastner M., and Ransom B. (2002). Elemental and isotopic chloride geochemistry and fluid flow in the Nankai Trough. *Geophys. Res. Lett.* **29**, 6-1–6-4.
- Srodon J. (1999) Nature of mixed-layer clays and mechanisms of their formation and alteration. *Ann. Rev. Earth Planet. Sci.* **27**, 19–53.
- Staudacher T. and Allègre C. J. (1988) Recycling of oceanic crust and sediments: the noble gas subduction barrier. *Earth Planet. Sci. Lett.* **89**, 173–183.
- Staudigel H. and King S. D. (1992) Ultrafast subduction: the key to slab recycling efficiency and mantle differentiation? *Earth Planet. Sci. Lett.* **109**, 517–530.
- Staudigel H., Plank T., White W. M., and Schminke H.-U. (1996) Geochemical fluxes during seafloor alteration of the upper oceanic crust: DSDP Sites 417 and 418. In *Subduction: Top to Bottom* (eds. G. E. Bebout, D. W. Scholl, S. H. Kirby, and J. P. Platt), Am. Geophys. Un. Geophys. Monogr. AGU, Washington, DC, vol. 96, pp. 19–38.
- Stern R. J. (2002) Subduction zones. *Rev. Geophys.* **40** (4), 1012, doi:10.1029/2001RG000108.
- Straub S. M. and Layne G. D. (2003) Decoupling of fluids and fluid-mobile elements during shallow subduction: evidence from halogen-rich andesite melt inclusions from the Izu arc volcanic front. *Geochem. Geophys. Geosyst.* **4**, doi:10.1029/2002GC000349.
- Sun S.-S. and McDonough W. F. (1989) Chemical and isotope systematics of oceanic basalts: implications for mantle composition and processes, In *Magmatism in the Ocean Basins* (eds. A. D. Saunders and M. J. Norry). Geol. Soc. Lond., pp. 313–345.
- Tanaka R. and Nakamura E. (2005) Boron isotopic constraints on the source of Hawaiian shield lavas. *Geochim. Cosmochim. Acta* **69**, 3385–3399.
- Tanimoto M. (2003) Petrology and geochemistry of the Horoman peridotite complex, Hokkaido, northern Japan. MS Thesis, University of Okayama at Misasa, Misasa, Japan, 51pp.
- Tatsumi Y. (2005) The subduction factory: how it operates in the evolving Earth. *GSA Today* **15**, 4–10.
- Tatsumi Y. and Kogiso T. (1997) Trace element transport during dehydration processes in the subducted oceanic crust. 2: Origin of chemical and physical characteristics in arc magmatism. *Earth Planet. Sci. Lett.* **148**, 207–221.
- Tenthorey E. and Hermann J. (2004) Composition of fluids during serpentinite breakdown in subduction zones: evidence for limited boron mobility. *Geology* **32**, 865–868.
- Tomaschak P. B., Widom E., Benton L. D., Goldstein S. L., and Ryan J. G. (2002) The control of lithium budgets in island arcs. *Earth Planet. Sci. Lett.* **196**, 227–238.
- Touret J. L. R. and Frezzotti M.-L. (2003) Fluid inclusions in high pressure and ultrahigh pressure metamorphic rocks. In *Ultrahigh Pressure Metamorphism* (eds. D. A. Carswell and R. Compagnoni). Eotvos University Press, Budapest, pp. 467–487.
- Tribuzio R., Messiga B., Vannucci R., and Bottazzi P. (1996) Rare earth element redistribution during high-pressure-low-temperature metamorphism in ophiolitic Fe-gabbros (Liguria, northwestern Italy): implications for light REE mobility in subduction zones. *Geology* **24**, 711–714.
- Tricart P. and Lemoine M. (1991) The Queyras ophiolite west of Monte Viso (Western Alps): indicator of a peculiar ocean floor in the Mesozoic Tethys. *J. Geodynam.* **13**, 163–181.
- Tsujimori T., Sisson V. B., Liou J. G., Harlow G. E., and Sorensen S. S. Very-low-temperature record of the subduction process: a review of worldwide lawsonite eclogites. *Lithos.* (in press).
- Usui T., Kobayashi K., Nakamura E., and Helmstaedt H. Trace element fractionation in deep subduction zones inferred from lawsonite-eclogite xenolith from the Colorado Plateau. *Chem. Geol.* (in press).
- Usui T., Nakamura E., and Helmstaedt H. (2006) Petrology and geochemistry of eclogite xenoliths from the Colorado Plateau: implications for the evolution of subducted oceanic crust. *J. Petrol.* **47**, 929–964.
- Usui T., Nakamura E., Kobayashi K., Maruyama S., and Helmstaedt H. (2003) Fate of the subducted Farallon plate inferred from eclogite xenoliths in the Colorado Plateau. *Geology* **31**, 589–592.
- van der Klauw S. N. G. C., Reinecke T., and Stockhert B. (1997) Exhumation of ultrahigh-pressure metamorphic oceanic crust from Lago di Cignana, Piemontese zone, Western Alps: the structural record in metabasites. *Lithos* **41**, 79–102.
- van Keken P. E., Kiefer B., and Peacock S. M. (2002) High-resolution models of subduction zones: implications for mineral dehydration reactions and the transport of water into the deep mantle. *Geochem. Geophys. Geosyst.* **3**, 1056, doi:10.1029/2001GC000256.

- Vrolijk P. (1990) On the mechanical role of smectite in subduction zones. *Geology* **18**, 703–707.
- Vrolijk P., Myers G., and Moore J. C. (1988) Warm fluid migration along tectonic mélanges in the Kodiak accretionary complex, Alaska. *J. Geophys. Res.* **93**, 10313–10324.
- Wei C. and Powell R. (2004) Calculated phase relations in high-pressure metapelites in the system NKFMAH ($\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$). *J. Petrol.* **45**, 183–202.
- Whitney D. L. and Davis P. B. (2006) Why is lawsonite eclogite so rare? Metamorphism and preservation of lawsonite eclogite, Sivrihisar, Turkey. *Geology* **34**, 473–476.
- Widmer T. and Thompson A. B. (2001) Local origin of high pressure vein material in eclogite facies rocks of the Zermatt-Saas zone, Switzerland. *Am. J. Sci.* **301**, 627–656.
- Widom E., Kepezhinskas P., and Defant M. (2003) The nature of metasomatism in the sub-arc mantle wedge: evidence from Re–Os isotopes in Kamchatka peridotite xenoliths. *Chem. Geol.* **196**, 283–306.
- Wiesli R. A., Taylor L. A., Valley J. W., Tromsdorff V., and Kurosawa M. (2001) Geochemistry of eclogites and metapelites from Trescolmen, Central Alps, as observed from major and trace elements and oxygen isotopes. *Int. Geol. Rev.* **43**, 95–119.
- Williams L. B., Hervig R. L., and Hutcheon I. (1999) Boron isotope geochemistry during diagenesis. Part II: Applications to organic-rich sediments. *Geochim. Cosmochim. Acta* **65**, 1783–1794.
- Woodland S. J., Pearson G., and Thirlwall M. F. (2002) A platinum group element and Re–Os isotope investigation of siderophile element recycling in subduction zones: comparison of Grenada, Less Antilles Arc, and the Izu-Bonin Arc. *J. Petrol.* **43**, 171–198.
- Wunder B., Meixner A., Romer R. L., and Heinrich W. (2006) Temperature-dependent isotopic fractionation of lithium between clinopyroxene and high-pressure hydrous fluids. *Contrib. Mineral. Petrol.* **151**, 112–120.
- Wunder B., Meixner A., Romer R. L., Wirth R., and Heinrich W. (2005) The geochemical cycle of boron: constraints from boron isotope partitioning experiments between mica and fluid. *Lithos* **84**, 206–216.
- Yamamoto J., Maruyama S., Parkinson C. D., and Katayama I. (2002) Geochemical characteristics of metabasites from the Kokchetav Massif: subduction zone metasomatism along an intermediate geotherm. In *The Diamond-Bearing Kokchetav Massif, Kazakhstan* (eds. C. D. Parkinson, I. Katayama, J. G. Liou, and S. Maruyama). Universal Academy Press, Tokyo, Japan, pp. 363–372.
- You C.-F., Castillo P. R., Gieskes J. M., Chan L. H., and Spivack A. J. (1996) Trace element behavior in hydrothermal experiments: implications for fluid processes at shallow depths in subduction zones. *Earth Planet. Sci. Lett.* **140**, 41–52.
- You C.-F., Gieskes J. M., Lee T., Yui T.-F., and Chen H.-W. (2004) Geochemistry of mud volcano fluids in the Taiwan accretionary prism. *Appl. Geochem.* **19**, 695–707.
- You C.-F., Spivack A. J., Gieskes J. M., Rosenbauer R., and Bischoff J. L. (1995) Experimental study of boron geochemistry: implications for fluid processes in subduction zones. *Geochim. Cosmochim. Acta* **59**, 2435–2442.
- Zack T., Foley S. F., and Rivers T. (2002) Equilibrium and disequilibrium trace element partitioning in hydrous eclogites (Trescolmen, Central Alps). *J. Petrol.* **43**, 1947–1974.
- Zack T., Rivers T., Brumm R., and Kronz A. (2004) Cold subduction of oceanic crust: implications from a lawsonite eclogite from the Dominican Republic. *Eur. J. Mineral.* **16**, 909–916.
- Zack T., Rivers T., and Foley S. F. (2001) Cs–Rb–Ba systematics in phengite and amphibole: an assessment of fluid mobility at 2.0 GPa in eclogites from Trescolmen, Central Alps. *Contrib. Mineral. Petrol.* **140**, 651–669.
- Zack T., Tomascak P. B., Rudnick R. L., Dalpe C., and McDonough W. F. (2003) Extremely light Li in orogenic eclogites: the role of isotope fractionation during dehydration in subducted oceanic crust. *Earth Planet. Sci. Lett.* **208**, 279–290.
- Zhang L., Ellis D. J., Arculus R. J., Jiang W., and Wei C. (2003) “Forbidden zone” subduction of sediments to 150 km depth—the reaction of dolomite to magnesite + aragonite in the UHPM metapelites from western Tianshan, China. *J. Meta. Geol.* **21**, 523–529.
- Zhang R. Y. and Liou J. G. (1996) Significance of coesite inclusions in dolomite from eclogite in the southern Dabie mountains China. *Am. Mineral.* **80**, 181–186.
- Zheng Y. and Kastner M. (1997) 12. Pore-fluid trace metal concentrations: implications for fluid–rock interactions in the Barbados accretionary prism. In *Proc. Oc. Drill. Prog., Sci. Res.* (eds. T. H. Shipley, Y. Ogawa, P. Blum and J. M. Bahr). vol. 156, pp. 163–170.
- Zheng Y.-F., Fu B., Gong B., and Li L. (2003) Stable isotope geochemistry of ultrahigh pressure metamorphic rocks from the Dabie-Sulu orogen in China: implications for geodynamics and fluid regime. *Earth-Sci. Rev.* **62**, 105–161.
- Zheng Y.-F., Fu B., Li Y., Xiao Y., and Shuguang Li. (1998) Oxygen and hydrogen isotope geochemistry of ultrahigh-pressure eclogites from the Dabie Mountains and the Sulu terrane. *Earth Planet. Sci. Lett.* **155**, 113–129.
- Zimmer M. M., Fischer T. P., Hilton D. R., Alvarado G. E., Sharp Z. D., and Walker J. A. (2004) Nitrogen systematics and gas fluxes of subduction zones: insights from Costa Rica volatiles. *Geochem. Geophys. Geosyst.* **5**, Q05J11, doi:10.1029/2003GC000651.
- Zindler A. and Hart S. (1986) Chemical geodynamics. *Ann. Rev. Earth Planet. Sci.* **14**, 493–571.