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6 Fluid and Mass Transfer at Subduction Interfaces—The Field
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ABSTRACT

The interface between subducting oceanic slabs and the hanging wall is a structurally and lithologically complex region. Chemically disparate lithologies (sedimentary, mafic and ultramafic rocks) and mechanical mixtures thereof show heterogeneous deformation. These lithologies are tectonically juxtaposed at mm to km scales, particularly in more intensely sheared regions (mélange zones, which act as fluid channelways). This juxtaposition, commonly in the presence of a mobile fluid phase, offers up huge potential for mass transfer and related metasomatic alteration. Fluids in this setting appear capable of transporting mass over scales of kms, along flow paths with widely varying geometries and P - T trajectories. Current models of arc magmatism require km-scale migration of fluids from the interface into mantle wedge magma source regions and implicit in these models is the transport of any fluids generated in the subducting slab along and ultimately through the subduction interface. Field and geochemical studies of high- and ultrahigh-pressure metamorphic rocks elucidate the sources and compositions of fluids in subduction interfaces and the interplay between deformation and fluid and mass transfer in this region.

Recent geophysical studies of the subduction interface — its thickness, mineralogy, density, and H_2O content — indicate that its rheology greatly influences the ways in which the subducting plate is coupled with the hanging wall. Field investigation of the magnitude and styles of fluid-rock interaction in metamorphic rocks representing “seismogenic zone” depths (and greater) yields insight regarding the roles of fluids and elevated fluid pore pressure in the weakening of plate interface rocks and the deformation leading to seismic events. From a geochemical perspective, the plate interface contributes to shaping the “slab signature” observed in studies of the composition of arc volcanic rocks. Understanding the production of fluids with hybridized chemical/isotopic compositions could improve models aimed at identifying the relative contributions of end-member rock reservoirs through analyses of arc volcanic rocks. Production of rocks rich in hydrous minerals, along the subduction interface, could stabilize H_2O to great depths in subduction zones and influence deep-Earth H_2O cycling. Enhancement of decarbonation reactions and dissolution by fluid infiltration facilitated by deformation at the interface could influence the C flux from subducting slabs entering the sub-arc mantle wedge and various forearc reservoirs.

In this paper, we consider records of fluid and mass transfer at localities representing various depths and structural expressions of evolving paleo-interfaces, ranging widely in structural character, the rock types involved (ultramafic, mafic, sedimentary), and the rheology of these rocks. We stress commonalities in styles of fluid and mass transfer as related to deformation style and the associated geometries of fluid mobility at subduction interfaces. Variations in thermal structure among individual margins will lead to significant differences in not only the rheology of subducting rocks, and thus seismicity, but also the profiles of devolatilization and melting, through the forearc and subarc, and the element/mineral solubilities in any aqueous fluids or silicate melts that are produced. One key factor in considering fluid and mass transfer in the subduction interface, that influences C cycling and chemical additions to arcs, is the uncertain degree to which sub-crustal, hydrated ultramafic rocks in downgoing slabs release H₂O-rich fluids.

Keywords: subduction; subduction interface; earthquakes; fluid flow; mass transfer; metasomatism; mélangé; high-pressure metamorphism

1. Introduction

The interface between subducting oceanic lithosphere and its hanging wall is generally viewed as a structurally and lithologically complex region within and through which fluids from various slab sources are transported (see the sketch in **Fig. 1**). In this region, large differences in rheology can lead to complex structural juxtaposition of disparate lithologies in a fluid-rich setting, leading to mass transfer and related metasomatic alteration (Bebout, 2013). These fluids are generated by devolatilization reactions at greater depths along the interface and in underlying sediment sections, the altered oceanic crust section, and possibly also hydrated and potentially carbonated sub-crustal ultramafic rocks in slabs (see Ranero et al., 2003; 2005; Faccenda et al., 2009; Emry and Wiens, 2015). In forearcs, the complex interplay of deformation and fluid flow makes the interface a major channelway for fluids released by mechanical expulsion and

devolatilization to migrate up-dip toward the seafloor, often leaving in their paths complex vein networks and other metasomatic features (see descriptions of veining by Fisher and Byrne, 1990; Bebout and Barton, 1993; Fisher et al., 1995; Breeding and Ague, 2002; Sadofsky and Bebout, 2003; Bachmann et al., 2009; Raimbourg et al., 2015). Fluids (including possible silicate melts) emanating from the interface and entering the mantle wedge could convey geochemical signatures of closely juxtaposed, disparate rock types and “hybridized” rocks having chemical/isotopic characteristics inherited from multiple metasomatized end-member lithologies (sediment, basalt/gabbro, peridotite; Bebout and Barton, 2002; King et al., 2006, 2007; Spandler et al., 2008; Marschall and Schumacher, 2012; Bebout, 2014; see **Fig. 1**). If it occurs at sub-arc depths, this hybridization could obscure efforts to deconvolute contributions of end-member slab fluid sources (basalt, sediment, slab peridotite) based on the chemical/isotopic compositions of arc lavas (see Bebout and Barton, 2002; King et al., 2006, 2007; Spandler et al., 2008; Marschall and Schumacher, 2012; Spandler and Pirard, 2013). Field studies of HP and UHP metamorphic suites consistently demonstrate the presence of relatively intact slabs or blocks of stronger materials separated by shear zones of varying scales and, in some cases, intensely sheared matrices. It appears unlikely that a deeply subducted lithosphere section would completely retain its stratigraphy from the seafloor (see **Fig. 1**). In fact, it is likely that there is even greater complexity and structural/lithological diversity of interfaces related to (1) subduction erosion (von Huene and Scholl, 1991; Clift and Vannucchi, 2004), (2) accretion/underplating (Platt, 1986; Angiboust et al., 2014a), (3) subduction of asperities (e.g., seamounts; Cloos, 1992), and (4) incipient continental subduction (Cloos, 1993; Scholl and von Huene, 2010).

Geophysical studies have increasingly focused attention on the possible seismic expressions of a subduction channel at the tops of subducting slabs (Hacker et al., 2003a,b; Abers, 2005;

Abers et al., 2006, 2009; Essen et al., 2009; Kim et al., 2013; Friedrich et al., 2014) and the ways in which interface mechanical properties relate to fluid generation and flow over a wide range of depths (see **Fig. 2**, from Audet and Bürgmann, 2014; also see Calahorra et al., 2008; Bachmann et al., 2009; Audet et al., 2009; Abers et al., 2013; Moreno et al., 2014; Saffer and Wallace, 2015). Recent work by field geologists has begun to connect metamorphic rock records of subduction interface fluid processes with the geophysical record, with emphasis on understanding deformation and fluid processes in seismogenic zones and at greater depths (see **Fig. 3**, from Angiboust et al., 2014a; see Rowe et al., 2005; John and Schenk, 2006; Vannucchi et al., 2008; John et al., 2009; Bachmann et al., 2009; Yamaguchi et al., 2012; Wassmann and Stöckhert, 2012, 2013; Andersen et al., 2014; Deseta et al., 2014; Fisher and Brantley, 2014; Whitney et al., 2014; Plunder et al., 2015). Fluids are known to play key roles in deformation and mass transfer in shear zones (e.g., Selverstone et al., 1991; Dipple and Ferry, 1992; Axen et al., 2001; Barnes et al., 2004; Keller et al., 2004; Goncalves et al., 2012). Rocks floating as distinct blocks within large expanses of weaker matrix (e.g., Catalina Schist, New Caledonia, Syros) may exhibit fracturing and brecciation, and related fluid-rock interaction greater than that exhibited by rocks in larger intact regions (Bebout, 2013; Angiboust et al., 2014b).

In this review article, we provide a synthesis of geological, geochemical, geophysical, and theoretical observations aimed at understanding the processes attending metamorphism along the forearc-to-subarc subduction interface (~15 to 120 km), with an emphasis on fluid transport processes and related mass transfer in various structural settings at the interface. We have chosen the suites discussed in this synthesis because they are representative of the features observed, and processes inferred, for the range of subduction depths considered along the subduction interface. We emphasize that, over some depth ranges, the set of processes operating can be reconciled as

being common among the various suites/settings and that many of the differences in conclusions made by previous authors, regarding fluid processes, relate to the scales at which the key observations were made and to which part of an evolving subduction interface is being investigated (see **Fig. 1**).

We argue that, because of the tendency for deformation to focus fluid processes (and any related mass transfer), any fluids emanating from subducting slab sections will tend to disproportionately bear geochemical signatures of such intensely deformed zones and not of the more intact expanses of relatively undeformed rock behaving largely as closed systems with respect to fluid-rock interaction. The estimated compositions of slab fluid components contributing to the generation of volcanic rocks are, in general, compatible with the likely compositions of such fluids (e.g., King et al., 2006, 2007; Spandler et al., 2008; Miller et al., 2009; Marschall and Schumacher, 2012; Spandler and Pirard, 2013). We explore the degree to which the subduction interface beneath arcs can be regarded as a major chemical reaction zone leading to the release of fluids with hybridized geochemical compositions and resulting in significant change in the compositions of rocks subducted into deeper parts of the mantle beyond subarc depths. The combination of this juxtaposition of disparate lithologies, in an actively deforming and fluid-rich setting, as slab sections are heated to $>600^{\circ}\text{C}$ (leading to their increased ability to transport mass), make subarc subduction interfaces (distances to tops of slabs beneath arc volcanoes are 72-173; global mean 105 km; Syracuse and Abers, 2006) a key location for understanding the evolution of major Earth reservoirs such as the lithospheric mantle, continental crust, and the mantle. We discuss the impacts of metamorphic reactions in this depth interval on geochemical cycling, including the possibility that the combination of intense mechanical mixing, fluid infiltration, and higher temperatures at the interface at these

depths could result in the release of C, via some combination of decarbonation and carbonate dissolution, in quantities capable of balancing outputs of C in arc volcanic gases (see the related discussion in Collins et al., 2015).

2. Rock Types Involved at the Subduction Interface

In general, materials at the subduction interface are derived from the subducting slab, the overlying plate, and the accretionary wedge. Materials derived from the subducting plate are crustal rocks including deep-sea sedimentary rocks, oceanic basalts and gabbros, and peridotitic rocks of the underlying lithospheric mantle. Materials derived from the overlying plate may include off-scraped sedimentary rocks and mantle wedge peridotite or serpentinite, and in some cases continental crustal rocks. Accretionary wedge materials include sedimentary rocks formed from sediments derived dominantly from the overlying plate.

Sedimentary rock types found in subduction metamorphic complexes include metacherts, metapelites, metagraywackes, metaconglomerates, and metacarbonates. These rocks are commonly disaggregated and mixed with other lithologies due to processes occurring within subduction zones and upon exhumation. Much of what we know about sedimentary rocks entering subduction zones comes from studies of material drilled from oceanic crust. The global subducting sediment (GLOSS) is estimated to contain ~17% biogenic components (7% is marine carbonate and 10% is biogenic silica), and it is estimated that 76% of the material is derived from terrigenous sediments (Plank and Langmuir, 1998; Plank, 2014).

Sedimentary rocks can be enriched in large ion lithophile elements (LILE; e.g., K, Rb, Cs, Ba) and other elements such as Li, B, Pb, C and N relative to other rock types within subduction zones. They also have high $\delta^{18}\text{O}$ values relative to the majority of the mafic and ultramafic

materials entering subduction zones. The concentrations of these elements and isotopic signatures have been used to trace sedimentary-derived metamorphic fluids within the subduction interface (e.g. Bebout and Barton, 1989, 1993; Bebout 1991a, b; Bebout and Fogel, 1992; Bebout et al., 1999; King et al., 2006, 2007; Penniston-Dorland et al., 2012a).

Metamorphosed mafic rocks are found in most subduction-related metamorphic complexes. These can include metamorphosed basalts and diabases whether formed at a mid-ocean ridge (MORB), as part of an oceanic island (OIB) or plateau, or derived from subducted arc volcanic rocks. MORB also commonly experiences hydrothermal alteration on the seafloor, and altered MORB exhibits variable enrichments (relative to fresh MORB) in K, Rb, Cs, Li, Cl, CO₂ and H₂O and local enrichments in Fe, Ba, Th and U, and local depletions in Mg and Ni (Alt and Teagle, 2003; Jarrard, 2003; Staudigel, 2014). Metamorphosed gabbroic rocks are found in some subduction-related complexes, including Fe-Ti gabbros (Philippot and Selverstone, 1991; Nadeau et al., 1993).

Metamorphosed ultramafic rocks, including serpentinite, are found in most subduction-related metamorphic complexes. In addition to occurring as massive serpentinite bodies or serpentinite blocks, they are also a common component of the fine-grained matrix found within many mélangé zones. Subduction-related peridotitic rocks could have originated in one of two general settings: as seafloor-altered peridotite of the subducting plate or from the hydrated mantle wedge of the overlying plate (Hattori and Guillot, 2007). Peridotite in the subducting slab may have been unroofed on the ocean floor at slow spreading ocean ridges by faulting. Peridotite is also exposed in rift valleys, transform faults and propagating rifts on fast spreading ridges, and peridotite massifs of large areal extent on the ocean floor (Snow and Dick, 1995). In these settings, it is subjected to serpentinization as it is exposed to and infiltrated by seawater.

Venting of serpentinizing fluids can lead to lithification of calcareous ooze, which fills fractures in serpentinite which may lead to the formation of ophicarbonates (Schroeder et al., 2002). Bending-related faulting of the subducting plate as it enters the trench cuts deep into the mantle also promotes hydration of crust and mantle on the downgoing plate (Ranero et al., 2003). Understanding the derivation of subduction-related peridotitic rocks has implications for understanding processes of interaction between plates. However, the tectonic setting of peridotitic protoliths can be a potentially difficult question to address. Major element chemistry alone may not be helpful in discriminating between mantle wedge and abyssal serpentinite (Deschamps et al., 2013). Trace element chemistry, including variations in REE patterns, has been used by some to discern between mantle wedge and oceanic lithospheric peridotite (e.g., John et al., 2010; Barnes et al., 2013), however there is much overlap in REE patterns among the different tectonic settings and ultramafic rock types (Deschamps et al., 2013). Most studies agree that Cr# of relict spinel appears to discriminate effectively between mantle wedge serpentinite and abyssal serpentinite (Barnes et al., 2013; Deschamps et al., 2013; Xie et al., 2013). It is clear that care must be taken in geochemical interpretation of serpentinite protoliths.

Seafloor altered serpentinites can carry H, C, and S into subduction zones. Evidence suggests that H₂O and S may be released from serpentinites due to devolatilization reactions during subduction metamorphism while C remains unaffected (Alt et al., 2013). While serpentinized oceanic peridotites account for less than 3% of the total subduction budget for C and S, these elements are isotopically fractionated and can be recycled into the mantle (Alt et al., 2013).

3. Pressure-Temperature Conditions along the Subduction Interface

Materials entering subduction zones encounter increasing pressure and temperature at depth along a notably cooler geotherm compared to typical geothermal gradients as is witnessed by the unique high-pressure/low-temperature minerals (e.g. omphacite, glaucophane, lawsonite) found in exhumed rocks (e.g., Ernst, 1972). The P - T conditions experienced by rocks along the subduction interface have profound implications for both their physical and chemical properties and therefore for the deformation style and behavior of rocks during subduction, and for elemental solubility, volatile release, and mass transfer associated with subduction. The deformation behavior of rocks changes as a function of pore fluid pressure, temperature, strain rate and pressure. Brittle deformation, including faulting, dominates at shallow levels within subduction zones. Ductile deformation occurs at higher temperatures by deformation mechanisms such as dislocation creep and dissolution precipitation creep. In the ductile regime, the rheology of rocks is dominantly affected by temperature and strain rate. Kirby et al. (1996) demonstrated a strong dependence of the earthquake records of modern subduction zones strongly tied to the thermal structure of the margins, relating this to temperature-dependent rheology.

Computational geodynamic models (e.g., Gerya et al., 2002; Syracuse et al., 2010) use observations such as seismic data, spreading rates and heat flow to provide predictions of the thermal structure of subduction zones that can be tested by comparison with evidence from subduction-related metamorphic rocks. A recent study comparing peak- P P - T conditions recorded by HP metamorphic suites indicates that these models produce temperatures too low for the forearc region (Penniston-Dorland et al., 2015). In Penniston-Dorland et al. (2015), estimates of temperatures at the peak pressures of metamorphism were compiled from the literature from exhumed blueschists, eclogites, and associated subduction-related metamorphic rocks from

around the world and compared to predictions of the thermal structure of subduction zones from computational geodynamic models. While the comparison is favorable at high P , at pressures for the forearc region ($P_{max} < 2$ GPa), the models predict temperatures that are on average 100-300 °C cooler than those recorded by exhumed rocks. This relationship can in general be seen in **Fig. 4**, in which peak P - T conditions estimated for the subduction interface localities considered in this paper (see **Table 1**), but not necessarily at peak P , are plotted along with prograde P - T paths calculated using geodynamic models for the range of active subduction zones (green lines, Syracuse et al., 2010) and for a range of parameters (plate age, velocity, dip, etc.) for incoming plates (red lines, Gerya et al., 2002). These conclusions are further supported by comparison of prograde P - T paths recorded by exhumed metamorphic rocks in the same compilation to the geodynamic modeling predictions (see Fig. 6 in Penniston-Dorland et al., 2015).

The thermal structure of subduction zones provides an important control on the cycling of elements, as heat is a major driver of devolatilization reactions during subduction metamorphism (e.g., Hacker, 2008). Models also provide the basis for quantitative estimates of geochemical cycling among Earth reservoirs of elements and compounds of great importance such as H₂O and CO₂ (e.g., Gorman et al., 2006; van Keken et al., 2011). If models underestimate temperatures experienced within subduction zones, taking H₂O as an example, far more H₂O is released during subduction at shallower levels, and far less H₂O can be recycled into the mantle (see Hacker, 2008; van Keken et al., 2011, Penniston-Dorland et al., 2015). Many elements/minerals would be expected to show different solubility relations in H₂O-rich fluids at somewhat higher temperatures, potentially strongly influencing the mass transfer occurring along subduction interfaces (and within subducting slab sections).

4. Mechanisms for Mass Transfer at the Subduction Interface

In this section, we provide a brief discussion of the processes by which metasomatism is thought to occur in subduction zones (also see the discussions by Bebout and Barton, 1993; Bebout, 2013). The dramatically contrasting geochemical compositions of rock types found in the subduction interface (sedimentary, mafic, ultramafic, and mixtures thereof), and any fluids that are present, are the driving forces for significant changes in chemical composition (metasomatism) along the interface.

Generally speaking, alteration of the initial chemical composition of rocks can occur in several ways during metamorphism: 1) diffusion of elements across a chemical potential gradient (diffusion is usually more efficient within a fluid along grain boundaries than within a solid), 2) advection of elements dissolved in an infiltrating fluid (e.g. aqueous fluid, melt) traveling within fractures or in intergranular pore spaces, and 3) physical/mechanical mixing of materials with different initial compositions. The first two processes of chemical transfer rely on fluids and depend on the evolving porosity and permeability of the rocks during metamorphism. The third process involves a complex interaction between deformation and metasomatism (and related change in mineral assemblages). The three processes, when operating in concert, can lead to the production of so-called “hybrid” rock compositions with geochemical characteristics variably inherited from the diverse lithologies at the interface (i.e., sediments, altered oceanic crust, ultramafic rocks), shaping the chemical/isotopic compositions of fluids with which these rocks interact.

4.1. Diffusion

Diffusive mass transport across a chemical potential gradient can occur when two adjacent lithologies have significantly different chemical compositions. During “wet” metamorphism

rocks are commonly a heterogeneous medium – a rock composed of different mineral grains that are surrounded by an intergranular fluid. In this case, the “bulk” diffusion through the medium is commonly dictated by the diffusivity of fluid-mobile elements through the intergranular medium (Watson and Baxter, 2007). Usually, diffusive transport of these elements results in a smoothly varying profile in which the distance over which the concentration or isotopic composition varies is a function of the diffusivity of the element in the medium, characteristics of the medium such as porosity and tortuosity, and the amount of time over which diffusion has occurred. Evidence for diffusive transfer is found in subduction-related metamorphic rocks generally over small scales (distances of cms) in regions adjacent to rock layers in which fluid infiltration is inferred (Franciscan Complex; Penniston-Dorland et al., 2010) and adjacent to metamorphic veins (Tianshan; John et al., 2012). The length-scale of diffusive transfer yields information regarding the timescales of the diffusion (Penniston-Dorland et al., 2010; John et al., 2012).

4.2. Advection of mass in fluids (or melts)

Evidence for advection of mass by an infiltrating fluid takes many forms in subduction-related metamorphic rocks. The presence of abundant veins, metasomatic reaction zones often containing significant amounts of hydrous minerals, and deviations of major- and trace-element chemistry as well as stable isotope compositions from likely protolith compositions all provide evidence for fluid infiltration in subduction-related metamorphic rocks (e.g., Bebout and Barton, 1993; Sorensen et al., 1997; Breeding et al., 2004; van der Straaten et al., 2008, 2012; Miller et al., 2009; Penniston-Dorland et al., 2012a,b). Mass transport by advecting fluids can result in enrichment (or depletion) of elements being carried by the fluid in the rock along the path of the fluid. These changes are due to exchange between the fluid and minerals in the rock and/or

crystallization of new minerals in the presence of the fluid. This mechanism of mass transfer is expected to produce the largest-scale effects, as the flow of fluids carrying dissolved load could certainly be km-scale in this environment (see Bebout and Barton, 1989, 1993). Much of the quantitative basis for our understanding of fluxes of metamorphic fluids during subduction is based on modeling predictions, and there are few quantitative estimates of fluid fluxes based on evidence from subduction-related metamorphic rocks (see Zack and John, 2007; Ague, 2014). One estimate of subduction-related fluid fluxes of 10^4 - 10^5 m³_(fluid)/m²_(rock) was based on silica precipitation in veins in the Otago Schist, New Zealand (see Breeding and Ague, 2002) and is comparable in magnitude to estimates of fluid fluxes required to precipitate silica in veins during regional metamorphism in New England (Ferry, 1992; Ague, 1994, Penniston-Dorland and Ferry, 2008).

Mineral stability and solubility affect mass transport by fluids, and the subduction zone environment has a cooler geotherm relative to other tectonic environments, resulting in differing types of fluid chemistry and different fluid fluxes required for mass transfer (see discussion by Frezzotti and Ferrando, 2015). Thermodynamic modeling (Dolejs and Manning, 2010) suggests that fluid fluxes required for transport and deposition of quartz and calcite in veins are 1 to 2 orders of magnitude lower than those required for geothermal gradients typical of orogenic belts. At the high pressure conditions in subduction zones, “intermediate” fluids, with properties between H₂O and hydrous silicate melt may play a role in the transport of mass, however this phenomenon is likely less important than originally thought because critical curves for chemically complex fluids occur at higher *P* than for simple systems (see Manning, 2004).

4.3. Physical/mechanical mixing

Bebout and Barton (1989, 1993, 2002) and Sorensen and Grossman (1989) described a process by which rocks of strongly “hybridized” compositions can be derived in subduction interface settings in which several highly disparate rock endmembers are available (also see Spandler et al., 2008; Penniston-Dorland et al., 2012b; 2014; Marschall and Schumacher, 2012). In such settings, physical attenuation due to deformation, and in some cases shearing into the matrix, of rind materials with abundant sheet silicates, can result in juxtaposition of disparate compositions at hand-sample scales (see the discussion by Penniston-Dorland et al., 2014). Bebout and Barton (2002) observed that large volumes of the matrix of the amphibolite-grade *mélange* unit in the Catalina Schist resemble geochemically the reaction rind material developed at the boundaries of variably disaggregated tectonic block material and surround *mélange* matrix. The matrix compositions of relatively fluid-immobile elements are consistent with mixing of materials derived from mafic and ultramafic blocks in the *mélange* (e.g. Cr, Al, Os, Ir, Ru; Bebout and Barton, 2002; Penniston-Dorland et al., 2014). The process by which the matrix and reaction rinds form are likely a complex combination of infiltrative and diffusive fluid transport along with mechanical mixing that occurs progressively during prograde metamorphism.

5. Sources of Fluids at the Subduction Interface

The behavior of volatiles during subduction is of particular importance in governing the surface-to-mantle volatiles budget on Earth. H₂O is particularly significant since it serves as the major agent for distribution of elements along the subduction interface, traveling toward the surface along the subduction thrust or vertically into the overlying plate. Subduction of oceanic lithospheric plates initiates a continuum of metamorphic reactions that release fluids, transitioning from shallow realms in which fluids are mechanically expelled during compaction

and diagenetic reactions to deeper levels (>15 km) at which low-grade metamorphism can result in significant devolatilization. Metamorphic reaction histories can strongly depend on the *P-T* paths experienced by the rocks in subducting slab sections (see the examples of peak *P-T* conditions recorded by subduction interface rocks and slab-top *P-T* paths modeled for rocks subducting into selected modern margins in **Fig. 4**). Schmidt and Poli (2014) provide a review of the experimental and field evidence for the devolatilization history of the wide range of rock types present at the subduction interface.

Studies of devolatilization in metasedimentary suites comparing rocks at various metamorphic stages have indicated that, in relatively cool subduction margins, relatively little devolatilization occurs to depths approaching those beneath volcanic fronts (>90 km; Bebout et al., 1999, 2013). Bebout et al. (2013) suggested that up to only ~20 wt. % of the H₂O in deeply subducting metapelites in the W. Alps was lost during subduction to depths of ~90 km, along a *P-T* gradient of ~7-8°C/km (also see Busigny et al., 2003). This implies that a large fraction of the volatiles in these rocks remains to depths beneath arc volcanoes and that a significant fraction of the volatiles could be retained to beyond subarc regions and into the deeper mantle. Based on thermodynamic calculations (Kerrick and Connolly, 2001; Collins et al., 2015), it appears that far larger fractions of structurally bound H₂O are lost from metabasaltic rocks subducted to these depths. On balance it appears that the combination of deeply subducting sediment and basaltic rocks can release significant amounts of H₂O-rich fluid into the subduction interface.

There has been considerable debate recently regarding the flux of H₂O-rich fluid evolved via devolatilization of upper mantle rocks in subducting slabs. Bending of slabs just outboard of trenches (in the outer rise region) is believed to result in infiltration of the slabs by seawater, resulting in the hydration of ultramafic rocks of the slab upper mantle (Ranero et al., 2003; 2005;

Faccenda et al., 2009). However, uncertainties remain regarding the extent of hydration experienced by these rocks during slab bending (see the recent discussion by Emry and Wiens, 2015). Large amounts of fluids emanating from this ultramafic section could have profound implications for the fluid and mass transfer at the interface, into/within which fluids would be focused, particularly at greater depths (see **Fig. 1**). Dehydration of these sub-crustal ultramafic rocks could occur at extremely variable depths (~100-200 km), depending on the thermal structure of the margin (van Keken et al., 2011). The depth of this dehydration would also depend on the bulk rock composition of the ultramafic rocks (Padron-Navarta et al., 2010).

Theoretical studies by Hacker (2008) and van Keken et al. (2011) provided margin-by-margin assessments of H₂O subduction to varying depths in modern margins, which show a wide range of thermal states. The calculations by Hacker (2008) suggested that approximately one-third of the initially subducted H₂O, including pore waters, is subducted to beyond subarc regions, that is, entering the deeper mantle and available to contribute to its H₂O inventory. Both studies stressed the very large range of potential H₂O loss profiles and overall surface-to-mantle recycling efficiency resulting from the wide range in thermal structure of modern subduction margins.

6. Field Records of Subduction Interface Processes

In this paper, we consider records of fluid and mass transfer at localities representing various expressions of evolving paleo-interfaces, ranging widely in the abundance and structural character of varying rock types involved (ultramafic, mafic, sedimentary; see Whitney et al., 2014). We have chosen to focus on suites for which there are good field constraints and abundant observations related to fluid and mass transfer in order to place these rocks in the context of our

discussion of deformation-enhanced fluid and mass transfer. Following are brief descriptions of the records of fluid and mass transfer in these high-*P* metamorphic suites (in order of increasing depths of interface development; peak *P-T* and other relevant information regarding these localities provided in **Fig. 4** and **Table 1**).

6.1. Depths of <40 km

Shallow to intermediate depths in forearcs (<40 km) include sediment-rich, paleo-accretionary settings involving accretion/underplating and transient subduction interfaces. Some of these suites contain shear/mélange zones with tectonic blocks of mafic, ultramafic, and sedimentary compositions. There has been great interest in deformation and fluid processes in this depth interval because of the clear connections with the generation of seismicity (see **Figs. 2 and 3**; Bachmann et al., 2009; Yamaguchi et al., 2012; Angiboust et al., 2014a, 2015; Audet and Bürgmann, 2014; Fisher and Brantley, 2014).

Studies of fluid and mass transfer in these shallow complexes indicate the mobility of dissolved material resulting in the precipitation of quartz- and carbonate-bearing vein arrays (e.g., Meneghini et al., 2009). These certainly indicate the mobility of mass (and fluid) at some scale, but assessments of scales of fluid mobility using stable isotopes have been complicated by the cryptic nature of infiltration by fluids previously equilibrated with very similar rocks in these very thick sequences of largely sandstone-shale sequences (see Sadofsky and Bebout, 2001, 2004; Sakakibara et al., 2007; Raimbourg et al., 2015). Fisher and Brantley (1992) argued for local-scale derivation of abundant quartz in veins in the Kodiak Formation, Alaska, involving diffusion of the dissolved silica from the host-rocks into fractures. On the other end of the spectrum, a record of km-scale fluid transport was documented for the Catalina Schist with clear evidence for fluid infiltration in tectonometamorphic units of varying metamorphic grade,

including the mélange units from the lowest grade (lawsonite-albite and lawsonite-blueschist facies) to the highest grade (amphibolite facies; see Bebout and Barton, 1989; Bebout, 1991a).

Fluid flux at the very shallow levels of accretionary complexes involves the mechanical expulsion of pore waters. Hacker (2008) estimated that, on a global basis, 46% of the H₂O released in Earth's subduction zones is released by closure of pores. This flux of H₂O-rich fluid out of the shallow levels has been observed in deep-sea drilling of fault zones and as venting of fluids onto the seafloor. The fluids venting into the oceans bear signatures of organic breakdown (to produce CH₄), diagenetic mineral-fluid reactions, and to varying degrees show “freshening” attributed to contributions of low-salinity fluids produced by low-grade metamorphic dehydration reactions (see Mottl et al., 2004). These latter authors documented changes in pore fluid chemistry emanating from serpentinite seamounts across the Marianas forearc that seemingly reflect cross-forearc change in contributions due to diagenesis and low-grade metamorphism of the sedimentary sequence subducting into this margin (also see the discussion by Bebout, 2014). At deeper levels in accretionary complexes, and deeper within the subduction channel, devolatilization reactions generate the volatiles being expelled from the subducting slab.

6.1.1. Depths of < 30 km

6.1.1.1. Arosa Zone, Central Alps: Rocks of the Arosa Zone (Bachmann et al., 2009 and references therein) display block in matrix (both shale and serpentinite matrix) textures on a variety of scales (block sizes range up to several km) with sedimentary, metabasaltic, metagabbroic and serpentinite rocks derived from the lower plate and metamorphic basement and dolomite derived from the upper plate (see **Fig. 5**). Temperatures and pressures indicate relatively shallow (<30 km) depths within the subduction channel. The distribution of pseudotachylyte is interpreted to represent a zone of unstable slip between 200 and 300 °C. The

presence of veins within this same zone and continuing to greater depths is also related to rupture and failure possibly associated with seismic events (Bachmann et al., 2009). Veins are boudinaged and sheared, and the minerals filling veins are dominantly large, well-developed crystals of quartz and calcite. In places, dilatational jogs in veins display chaotic mineral growth, including fine-grained, dynamically recrystallized calcite.

6.1.1.2. Shimanto and Chichibu Belts, Japan: The Tertiary Shimanto Belt (Kimura et al., 2012) consists of a more coherent unit (Hiwasa) adjacent to two *mélange* units (Mugi) on the islands of Kyushu, Shikoku, and Honshu, Japan (see Yamaguchi et al., 2012). These *mélange* units are < 200 m thick and contain basalts, pelagic cherts, red shales, and hemipelagic shales in a scaly, black shale matrix. The *mélange* is interpreted as tectonic, and is thought to represent fault rock along the plate boundary. There are pseudotachylytes and cataclastic layers found in the Shimanto Belt that are thought to record evidence for various types of earthquake events. Quartz veins are found, in some cases along brittle faults, indicating late-stage fluid flow. Fluid inclusions in veins from the southern Shimanto belt are mostly water-rich, but appear to trap both H₂O and carbonic species, indicating temperatures between 215 and 255 °C and pressures of ~0.2 GPa (Lewis et al., 2000). The flow within the accretionary prism was driven by deformation, and the scale of that flow was relatively restricted (Lewis and Byrne, 2003). Fluid inclusions in veins from the northern Shimanto belt record somewhat lower temperatures ranging from 150-170 °C at pressures of ~ 0.1 GPa (Yamaguchi et al., 2012). Carbon, oxygen and strontium isotopes indicate that while some veins formed on the seafloor, others formed during faulting due to fluids derived from several different sources (shales, basalts, and seawater; Yamaguchi et al., 2012; see **Fig. 6**).

The Jurassic accretionary complex of the northern Chichibu belt in western Shikoku, Japan (Sakakibara et al., 2007) consists of low-grade metamorphosed or unmetamorphosed psammitic and pelitic rocks, chert, greenstones and limestone. In the Hijikawa unit, there are low-grade coherent schistose and chert units separated by small-scale thrusts and *mélange* units comprised of pelitic schist with lenses of chert and mafic schist that are sheared by faulting. Estimated temperatures for the Hijikawa unit are ~230-290 °C and pressures are ~0.5-0.6 GPa (Sakakibara et al., 2007). Oxygen isotopic compositions of veins and whole rocks were inferred to reflect up-dip flow of fluid derived from higher-temperature pelitic rocks at greater depths within the accretionary prism (Sakakibara et al., 2007).

6.1.1.3. Kodiak Islands, Alaska: The Kodiak Complex (Kodiak Island, Alaska) has alternating formations of *mélange* and relatively coherent low-grade (~200-300 °C) accretionary formation (Vrolijk et al., 1988; Fisher and Byrne, 1990). Adjacent to forearc rocks on the west side of Kodiak Island there is the ~2 km thick Uyak Complex which is *mélange* with greenstone, greywacke, gabbro and ultramafic blocks in a chert-argillite matrix. This *mélange* was interpreted to have a tectonic origin (Moore and Wheeler, 1978) based on lack of evidence for soft sediment deformation and evidence for foliation formed under significant confining pressure. Moving eastward, next is the Kodiak Formation consisting of thin-bedded turbidites and massive sandstone that is more coherent and only locally disrupted. Crack-seal quartz veins in the Kodiak Formation (see descriptions by Fisher and Brantley, 1992, 2014; Fisher et al., 1995; Fisher, 1996) may have been produced in episodes that lasted <10 days, a duration that is similar to the duration of some slow earthquakes in nature, suggesting that silica redistribution may play a role in determining the frequency of slip along the subduction interface (Fisher and Brantley, 2014). Further east is the ~4 km thick Ghost Rocks Formation which is a disrupted

mélange unit with sandstone and shale and occurrences of pillow basalt. Occurrence of pseudotachylyte and cataclasite in the Ghost Rocks Formation provide evidence for seismic activity on what is interpreted as a thrust surface (Rowe et al., 2005, 2011). Methane inclusions in quartz veins from both the Uyak and Ghost Rock Formations indicate decreasing pressures from the edge of the vein to the center which was interpreted as evidence for cycles of fluid buildup and release, which, over time, dropped the overall fluid pressure (Vrolijk, 1987a,b; Vrolijk et al., 1988).

6.1.2. Depths of 30-40 km

6.1.2.1. Franciscan Complex, California: Together, the Coastal, Central, and Eastern Belts of the Franciscan Complex provide a protracted history of accretion, underplating and transient development of subduction interfaces. Each of these major units contains a rich history of fluid-rock interaction, in the form of complex veining and, in more sheared mélange domains, evidence of metasomatic exchange among disparate lithologies. The O and C isotope compositions of carbonate-bearing veins (calcite or aragonite) and calculated fluid compositions using these compositions indicate that, while in some cases fluids may be derived from local host rocks, in other cases fluids were derived externally (**Fig. 7**; Sadofsky and Bebout, 2001, 2004). The Central Belt of the Franciscan Complex contains blueschists, eclogites and amphibolites as blocks in shaly and serpentinite matrix and also contains more intact, variably deformed blueschist terrains (several km thick and tens of km long; Cloos, 1986). Temperature and pressure estimates from more intact Franciscan metasedimentary rocks are ~200 °C and range from 2 to 8 kbar (Ernst, 2011, and references therein). The ‘exotic’ mafic blocks in matrix and associated Mg-rich reaction ‘rinds’ have been the focus of extensive study of fluid-rock interactions during subduction metamorphism. Such reaction rinds have been observed in many

other localities described below, and are inferred to represent fluid-assisted mixing of altered material from mafic blocks and an ultramafic matrix which is no longer present in many examples in the Franciscan (Sorensen and Grossman, 1993; Sorensen et al., 1997; Penniston-Dorland et al., 2010; Errico et al., 2013; Ukar and Cloos, 2013). Recent constraints on the maximum pressures and temperatures of metamorphism of high-grade blocks in the Franciscan range from values for low-*T* blueschists (~0.5-0.6 GPa, 300–350 °C; Ukar and Cloos, 2014) up to values for high-*P* eclogites (2-2.5 GPa and 550-620 °C; Tsujimori et al., 2006; Page et al., 2007). Evidence from the LILE and Li concentrations and isotopic compositions of mafic blocks and the O isotopic compositions of garnets within those blocks attests to interaction of the mafic block cores with fluids during subduction (Sorensen et al., 1997; Penniston-Dorland et al., 2010; Errico et al., 2013; Page et al., 2014). At one Franciscan exposure, a profile across the contact between eclogite and blueschist altered by fluids from eclogite demonstrates small-scale variability in Li concentrations and $\delta^7\text{Li}$ that are consistent with diffusion within the eclogite into the altered blueschist. Diffusion modeling suggests that the infiltration event that created the blueschist was relatively brief (<100 year; Penniston-Dorland et al., 2010).

6.1.2.2. Catalina Schist, California: The Catalina Schist exhibits a range of metamorphic grades from lawsonite-albite up to amphibolite facies (Grove and Bebout, 1995). Kilometer-scale regions of *mélange* (Bebout and Barton, 2002) are observed throughout the Catalina Schist, in which blocks of varying lithologies, including metasedimentary, metabasalt, and metaultramafic rocks, are surrounded by finer-grained matrix. The blocks exhibit a range of sizes up to hundreds of meters in diameter grading into regions that exhibit more coherent behavior. The most thorough work on *mélange* geochemistry to date has been on the amphibolite-facies *mélange* unit in the Catalina Schist (Sorensen and Barton, 1987; Sorensen,

1988; Sorensen and Grossman, 1989; Bebout and Barton, 1989, 1993, 2002; Bebout, 1991a; King et al., 2006, 2007; Penniston-Dorland et al. 2012a, 2014). The mélange matrix displays chemical compositions consistent with mechanical mixing of material derived from the blocks, but with some fluid-mediated removal and addition of elements, most conspicuously an addition of Si (Bebout and Barton, 2002, see **Fig. 8**). Evidence for extensive fluid-rock interactions during subduction comes from O, C, H, N, and Li analyses of veins, altered rocks and mélange matrix that suggest externally-derived fluids sourced from metasedimentary rocks infiltrated the rocks and altered their isotopic composition in some cases (e.g. O, see **Fig. 9**) homogenizing the isotopic composition on relatively large (km) scales (i.e., across all metamorphic grades), in other cases (e.g. N, Li) homogenizing the isotopic composition on intermediate scales (i.e. within a single metamorphic grade; Bebout, 1997; Penniston-Dorland et al., 2012a). Reaction rinds surrounding mafic blocks in mélange matrix exhibit evidence for a complex process of formation involving both mechanical mixing and fluid infiltration (Sorensen, 1988; Bebout and Barton, 2002; Penniston-Dorland et al., 2012b, 2014, see **Fig. 10**).

There are several reports of evidence for partial melting in subduction settings including for the Catalina Schist amphibolite unit (Sorensen and Barton, 1987), the Sierra del Convento mélange in Cuba (García-Casco et al., 2008; Lazaro and García-Casco, 2008), and the Mt. Hochwart mélange unit in Italy (Marocchi et al., 2010). All of these units experienced peak metamorphism at temperatures considerably warmer for the estimated depths than predicted by thermal models for subduction-related metamorphic rocks. However, these rocks provide some insight regarding the deeper high-*T* histories of rocks subducting along cooler *P-T* paths, as many reactions in the more ultramafic bulk compositions are fairly *P*-insensitive (see Kerrick and Connolly, 1998; Bebout and Barton, 2002; Spandler et al., 2008; Spandler and Pirard, 2013;

Collins et al., 2015) and the chlorite-, talc-, and amphibole-rich mineral assemblages are stable to far greater pressures.

6.1.2.3. Mt. Hochwart, Eastern Italian Alps: The Mount Hochwart locality (Marocchi et al., 2010) contains a *mélange* unit with lens-shaped bodies of peridotite found within garnet-kyanite-bearing gneisses. The peridotites are interpreted to have been fragments of mantle wedge incorporated into downgoing continental crust. Centimeter-thick metasomatic contact bands of variable thickness are found at the contact between peridotite and gneiss, in which relatively fluid-mobile elements (such as the LILE) are not observed to travel far into the peridotite. These results suggest limited mobility of these elements in situations where transport is not focused in fluid flow channels or veins. One exception is Li, which appears across all the metasomatic zones.

6.1.2.4. Dent Blanche-Sesia, Western Alps: The Dent Blanche Thrust Zone (Angiboust et al., 2014a, 2015) consists of upper plate gneisses underlain by ophiolitic rocks (Tsaté Complex) on the lower plate. At the interface of these two rock units, there are different types of regions exhibiting mixing and cataclasis (Angiboust et al., 2014a, 2015). The cataclasite zones occur in 1-100 m thick layers immediately below the overlying gneisses. The cataclasite incorporates gneiss fragments and also contains epidote-quartz veins in a matrix of fine-grained quartz, albite, epidote, titanite, phengite, chlorite and actinolite. In one locality, the Arolla Gneiss is underlain by a ~200 m wide serpentinite thrust zone containing metagabbro pods (see **Fig. 3**). *P-T-t* constraints from these rocks suggest progressive underplating and accretion of incoming material at 30-40 km depth along the subduction interface over time with the active subduction thrust migrating outboard over time (Angiboust et al., 2014a).

6.2. Depths of 40-90 km

The suites representing 40-90 km contain intensely sheared domains, with development of mélange zones in some localities that contain greater degrees of disaggregation of slab and hanging-wall rocks (and over a wide range of scales; e.g., Syros and Tinos, New Caledonia, Sesia Zone, Sivrihisar, Voltri Massif, Tianshan). Monviso represents an intraslab setting in which shear zones and fracture networks are developed in less deformed altered oceanic crust. Erro Tobbio and Cima di Gagnone contain ultramafic rock, in sheared/mélange zones, of subduction-zone peridotites, presumed to be either seafloor-altered or hanging-wall ultramafic rock. Hanging-wall rocks can also be previously underplated rocks of either oceanic or continental crustal affinities or they could conceivably be intact continental crust of the overlying plate.

6.2.1. Depths of 40-70 km

6.2.1.1. Sesia Zone: The Sesia Zone is distinct among the localities discussed here because it represents one of the largest bodies of continental crust subducted to depths of ~60-65 km. The lithologies include metapelitic rocks, metamorphosed calcareous pelites, and metagranitoids intercalated with smaller slices of metabasites and lenses of carbonate- and quartz-rich rocks (Compagnoni, 1977; Konrad-Schmolke et al., 2006). Nonetheless, these rocks exhibit evidence for extensive fluid and mass transport during their exhumation – while they were positioned above the dehydrating subducting slab (see Halama et al., 2014; Konrad-Schmolke and Halama, 2014).

Eclogite facies rocks contain subduction-related metamorphic minerals including garnet, omphacite, amphibole, and phengite that display evidence for partial equilibration along grain boundaries, brittle fractures and other fluid pathways (Konrad-Schmolke et al., 2011). Sharp and diffuse mineral compositional zoning in some cases reflects up to three different compositional

variations, and coupled with evidence from mineral replacement textures, suggests multiple influxes of fluid in individual samples. Overall, open-system, pervasive reactive fluids are thought to have infiltrated across large volumes of rock above the subducting slab (see Halama et al., 2014).

6.2.1.2. New Caledonia: The northeast end of New Caledonia contains subduction-related metamorphic rocks ranging from lawsonite-blueschist to eclogite facies (Spandler et al., 2003, 2004, 2008). While the lower grade rocks exposed on New Caledonia (the Diahot Blueschists) are relatively coherent tracts of sedimentary rocks with some intercalated basaltic and rhyolitic rocks, the higher-grade rocks exposed in the northeast display mixing of materials characteristic of *mélange* zones (see **Fig. 11**). This locality contains eclogite, garnet blueschist, and garnet amphibolite along with metamorphosed ultramafic rocks and metasedimentary rocks (quartz-garnet-mica schists). *Mélange* matrix consists of talc, chlorite, and phengite along with quartz clasts and coarse-grained amphibole clots, and is thought to have formed prior to or during peak metamorphism. Hybrid talc and chlorite schists formed due to metasomatism and mixing among mafic, metasedimentary, and ultramafic rocks in the *mélange* zone (Spandler et al., 2008). Recent work on veins in eclogite in this suite demonstrated a complex “drainage system” for fluids generated by dehydration reaction which metasomatized host-rocks (Taetz et al., 2015).

6.2.1.3. Tianshan, China: The Tianshan HP-LT belt occurs in NW China and contains blueschist, eclogite and greenschist facies metasedimentary rocks, mafic metavolcanic rocks, marbles and metamorphosed ultramafic rocks (Gao and Klemd, 2003; Klemd et al., 2011). Hosted within greenschist and blueschist units are lenses, pods and slices of blueschist, eclogite, marble, and ultramafic rocks, in classic *mélange* style. The Tianshan is the first locality where

primary fluids at the blueschist to eclogite transition were described (Gao and Klemd, 2001). These fluid inclusions were low salinity, H₂O-NaCl rich and were thought to represent fluids derived internally from the rocks during dehydration.

Alteration halos surrounding omphacite-quartz-calcite veins in blueschist show that eclogite veins formed due to infiltration of an externally-derived fluid (John et al., 2008; Beinlich et al., 2010; John et al., 2012). These fluids interacted with the host rock and removed REE, HFSE, some LILE (Cs, Rb, Ba, K) and Li from the host rock during the eclogitization process but added Ca, Sr, and Pb (see **Fig. 12**). A profile across the vein-host rock contact demonstrates small-scale variability in Li concentrations and $\delta^7\text{Li}$ that are consistent with diffusion into the eclogite. Diffusion modeling suggests that the infiltration event that created the vein was relatively brief (perhaps ~200 year; John et al., 2012).

6.2.1.4. Syros, Tinos: The Greek islands of Syros and Tinos contain *mélange* formations metamorphosed through the Eocene that are composed of eclogites, blueschists, metagabbros, serpentinites, metaplagiogranites, and metasedimentary rocks (Ague, 2007; Miller et al., 2009; Ague and Nicolescu, 2014; Pogge von Strandmann et al., 2015). The *mélange* matrix on Syros is in some places serpentinite and in others metasedimentary rock. Metasomatic exchange at lithologic contacts between *mélange* blocks and serpentinite matrix resulted in the development of asymmetric reaction rinds rich in omphacite, glaucophane, and/or chlorite on the edges of some mafic blocks. Two-dimensional numerical models of fluid flow within *mélange* matrix suggests that, as permeability decreases within blocks, flow is diverted around blocks into matrix leading to enhanced fluid-rock reaction at the block margins (Ague, 2007).

Multiple studies have observed changes in chemical composition in these rocks at interfaces between mafic, ultramafic, and metasedimentary rocks, resulting in ‘hybrid’ chemical

compositions of rocks and also inferred changes in fluid composition, resulting ultimately in transferring the chemical signature of these fluids and rocks to arc magmas or deep into the mantle (see **Fig. 13**; Breeding et al., 2004; Miller et al., 2009). Formation of reaction zones adjacent to veins in metacarbonate rocks produces chemical change including loss of CO₂ that suggest fluid infiltration from surrounding rocks resulting in dissolution of carbonate and precipitation of silicate minerals (Ague and Nicolescu, 2014). Although the volumetric significance of carbonate dissolution remains unknown, this fluid-rock interaction could provide a mechanism, in addition to decarbonation, for the release of large quantities of CO₂ from subducting slabs (see **Fig. 14**; Ague and Nicolescu, 2014; Collins et al., 2015).

6.2.1.5. Erro Tobbio and Voltri Units, Ligurian Alps: At this locality, ultramafic tectonic blocks occur within a matrix of tectonized ultramafic rocks (Scambelluri et al., 2001) and mafic and metasedimentary lenses are found in a chlorite-rich matrix (Federico et al., 2007). Major and trace-element metasomatism at the rims of the ultramafic blocks is interpreted to represent the effects of seafloor serpentinization, whereas the compositions of veins in the ultramafic rocks provide constraints on the composition of fluids released by dehydration reactions (Scambelluri et al., 2001). The compositions of the veins reflect enrichment of elements derived locally due to dehydration of serpentinite, suggesting lack of externally derived fluid infiltration, and the authors suggest that REE, Cl, Sr, some alkalis, in addition to H₂O, can be conveyed to great depths in subduction zones in such lithologies.

6.2.2. Depths of 70-90 km

6.2.2.1. Sivrihisar, Turkey: The Sivrihisar massif is part of the Tavsanli zone of central Turkey, which is one of the largest high-pressure/low-temperature belts (250 x 40 km) exposed on Earth (Whitney et al., 2014). Interlayered, deformed marbles, quartzites, and metabasalts are

continuously exposed on scales up to kilometers within the Sivrihisar massif. Elliptical lawsonite eclogite pods occur within blueschist, quartzite, and calc-schist ranging in size from 1 cm to 5 m. Many of these pods are folded and have millimeter-scale alternating layers of blueschist and eclogite at the margins. Additionally, pods and lenses of metatuff, metagabbro, and serpentinite occur surrounded by blueschist. Serpentinite lenses have reaction zones of chlorite-lawsonite $\pm$ talc $\pm$ oxides $\pm$ carbonate. Although a detailed study of fluid processes in these rocks has not yet been conducted, the presence of lawsonite-bearing and other veins seemingly reflects diverse fluid-rock interactions (Martin et al., 2014).

6.2.2.2. Monviso (Western Italian Alps): Extensive work on fluid-rock interactions has been conducted on rocks from this locality, beginning with Philippot and Selverstone (1991) and Nadeau et al. (1993), which focused on veins in Fe-Ti metagabbros in the Lago Superiore Unit at this locality. That work documented relatively closed-system fluid-rock behavior during the formation of these veins. Spandler et al. (2011) suggested early closed-system behavior, leading to vein formation, followed by open-system behavior, based on compositions of garnet and other vein phases, and proposed that dehydrating ultramafic rocks were the sources of this fluid.

More recently, Angiboust et al. (2011a,b; 2014b) placed the various eclogitic units, and intervening deformed ultramafic rocks, into the context of shearing at/near the subduction interface, suggesting that the Lower Shear Zone at Monviso represents an intraslab shear zone (see **Fig. 15**). Mafic eclogites near and within this shear zone are brecciated and variably metasomatized and the authors used a combination of garnet chemistry and whole-rock chemistry to document metasomatic exchange between the mafic and ultramafic lithologies, in a fluid-rich setting (**Fig. 15**). A more detailed, larger-scale study of fluid-rock interactions, using stable isotope data, has not yet been conducted at this locality.

6.2.2.3. Cima di Gagnone, Adula Unit, Swiss Central Alps: At Cima di Gagnone, pelitic schists and gneiss enclose chlorite harzburgite and garnet peridotite lenses, and Cannaó et al. (2015; also see Scambelluri et al., 2014) suggested that this unit represents a slab-top mélange (see **Fig. 16A**). These authors documented multiple hydration/dehydration events related to antigorite and chlorite breakdown. The fluids released by these reactions facilitated metasomatic interactions among the disparate lithologies in this mélange unit, as reflected in the redistribution of many trace elements and B and Pb isotopes. The scenario of mixing of mantle and crustal materials within the subduction interface that is invoked by these authors (see also Scambelluri et al., 2015) is similar to one model proposed by Spandler and Pirard (2013; see **Fig. 16B**) involving the production of a hydrated mélange zone at the top of a subducting slab, in this case largely containing ultramafic lithologies with smaller components of mafic and sedimentary rocks. These models both suggest mixing of mantle and crustal materials at the subduction interface and do not require the same large-scale transport of fluids and mass as is required if the mantle-derived component is sourced in the sub-oceanic lithospheric mantle. Fluids with compositions reflecting sediment sources and seafloor hydrothermal alteration, can be released from metasomatized ultramafic rocks along the subduction interface (Scambelluri et al., 2015).

7. Discussion

7.1. Common themes in mass transfer at the subduction interface

It is possible to draw some generalities from the metasomatic parageneses observed in rocks from the subduction interface and to infer some relative mobilities of major and trace elements in HP/UHP metamorphic fluids (also see Bebout and Barton, 1993; Dolejs and Manning, 2010; Bebout, 2013; Manning, 2014). Transfer of mass in H₂O-rich fluids is thought to vary

dramatically depending on the P - T path the fluids take, and the rocks encountered, once liberated from subducting slabs.

7.1.1. *Quartz $\pm$ calcite veining*

As predicted from solubility relations (see Manning, 1994), quartz solubility is sufficiently high that Si metasomatism can dominate the metasomatic record (also see Dolejs and Manning, 2010). Veins containing quartz, with or without carbonate (generally calcite or aragonite), are nearly ubiquitous in metasedimentary-dominated (ordinarily quartz-saturated) subduction interface rocks representing depths of <40 km, suggesting Si addition, and in some cases can make up a large fraction of the volume of an individual exposure (see Breeding and Ague, 2002, who also suggested removal of large amounts of Si by dissolution in the metasedimentary host rocks). In general, this deposition of quartz and carbonate is consistent with up-dip flow of fluid, that is, down- T and down- P and parallel to the subduction thrust (see path 1 in **Fig. 17**; see **Section 7.5.6**). Examples of suites discussed in this review containing such veins are Arosa, Franciscan, Shimanto, Kodiak Island, and Catalina Schist. Rocks in these suites commonly contain multiple generations of veins containing these minerals, showing cross-cutting relations and diverse textures relative to the deformation textures of the host-rocks (see Sadofsky and Bebout, 2004; Bachmann et al., 2009; Menenghini et al., 2009; Yamaguchi et al., 2009). In a smaller number of cases, these quartz-calcite veins also contain minerals that are part of the peak-metamorphic mineral assemblage of the host-rocks or minerals that are more clearly retrograde.

7.1.2. *Other silica metasomatism*

Fluid-rock interaction can result in either enrichment or depletion of silica depending on the fluid P - T paths, and the diverse rock compositions encountered along fluid flow paths, (see

Bebout and Barton, 1993; Manning, 1997; Dolejs and Manning, 2010; Bebout, 2013). Aqueous fluids containing appreciable dissolved Si through interaction with quartz-bearing metasedimentary rocks (see **Fig. 17**) would be expected to drop much of this silica when they interact with Si-poor lithologies with large ultramafic components. Thus the possibility exists for a fluid to change considerably in its dissolved Si (and other dissolved element load) along a complex *P-T* path involving traverses across widely disparate lithologies (see Bebout, 2013). For example, regional/km-scale addition of Si to amphibolite-grade *mélange* ultramafic rocks by fluids generated in lower-grade metasedimentary rocks in the Catalina Schist was documented by Bebout and Barton (2002) (see the evidence for Si addition to this *mélange* unit in **Fig. 8B**).

7.1.3. LILE metasomatism

The addition or removal of LILE, from rocks of varying bulk compositions, has been documented in a number of studies, particularly in studies of the metasomatism of rocks initially poor in these elements (e.g., ultramafic and mafic rocks). Bebout (2007) documented that many HP and UHP metabasaltic rocks, commonly occurring as tectonic blocks in sheared matrix, show whole-rock enrichments in LILE such as Ba, Rb, Cs, K, and Pb. Whole-rock enrichments in Ba and Pb can be most directly associated with subduction-zone metasomatism, as the other elements are also commonly enriched on the seafloor during interactions with seawater. This type of metasomatism can occur during both prograde and retrograde metamorphism. For example, Sorensen et al. (1997) documented addition of LILE to mafic rocks of the Catalina Schist and Samana Complex (Dominican Republic) associated with the addition of phengite and documented prograde and retrograde crystallization of the phengites (based on textural relationships) indicating multi-stage addition of LILE. Gabbroic and dioritic cobbles in blueschist-facies-metamorphosed conglomerates in the Catalina Schist similarly

show large co-enrichments of Cs, Rb, and Ba, along with enrichments in B and N (Bebout, 1997; 2013).

7.1.4. Na-rich metasomatic parageneses

Jadeitites (rocks rich in jadeite, Na-Al pyroxene) are found in subduction-related mélange in a range of localities around the world (see the review by Harlow et al., 2015). Jadeitite mineral textures suggest that in some cases these rocks crystallized from fluids in veins, and thereby their presence attests to transport of Na, Al, and Si by metamorphic fluids (e.g., Harlow and Sorensen, 2005; Cárdenas-Párraga et al. 2012). Evidence from jadeite that has been replaced dominantly by albite (albitites) in the Sierra de las Minas, Guatemala, suggests subsequent mobility of LILE (K, Rb, Cs, Ba, Sr, Pb) and also Hf, Zr, Th and U, all thought to be introduced by externally-derived fluids (Sorensen et al., 2010). Further evidence for the mobility of Na, Al, and Si is documented by the presence of sodic-amphibole-bearing veins and their alteration envelopes, and albite-rich veins, both found in blueschist facies metasedimentary rocks of the Catalina Schist (Bebout and Barton, 1993). In both the amphibolite-grade unit of the Catalina Schist and the Mt. Hochwart mélange unit, leucosomes and pegmatites largely tonalitic/trondhjemitic in composition reflect H₂O-saturated partial melting and mobilization of an “albitic component” (for the Catalina Schist, Sorensen and Barton, 1987; Bebout and Barton, 1993; Bebout, 2013; for Mt. Hochwart, Marocchi et al., 2010). Sorensen and Grossman (1989) suggested that some eclogite blocks in the Catalina Schist amphibolite-grade mélange experienced removal of an “albite component” likely in the form of partial melt.

7.1.5. Other trace element metasomatism along the subduction interface

The hierarchy of trace element mobilities at depth along the subduction interface more or less mimics the mobilities predicted by experimental studies (see experiments on aqueous fluid-

821 MORB by Kessel et al., 2005). In these and other experiments, trace elements with higher fluid-
822 solid partition coefficients include Cs, Rb, Ba, Sr, B, Li, Pb, Th and U, all of which are
823 commonly enriched in metasomatic products at the interface. Boron and Cs are sufficiently
824 partitioned into fluids during devolatilization of metasedimentary rocks to produce observable
825 loss (Bebout et al., 1999). The experiments by Kessel et al. (2005) indicate relative immobility of
826 HFSE such as Nb, Ta, Zr, and Hf, except at temperatures $>800^{\circ}\text{C}$, and the REE are also
827 relatively immobile but show increasing partitioning into fluids with decreasing atomic weight.
828 The increasing potential of higher- T aqueous fluids and supercritical/transitional fluids to
829 mobilize trace elements (see Hermann et al., 2006) is borne out by experiments of Kessel et al.
830 (2005), which show 1-2 orders of magnitude increase in fluid-MORB partitioning in these
831 higher- T fluids. In accordance with this experimental finding, elements such as the HFSE and
832 REE typically do not show evidence of their mobility, in the form of significant depletions in
833 devolatilized rocks, in HP and UHP interface rocks all peak-metamorphosed at temperatures
834 $<600^{\circ}\text{C}$. However, these elements certainly do occur in some veins and in metasomatic rinds on
835 tectonic blocks in mélangé units, indicating some mobility.

836 Evidence from metamorphosed basaltic rocks from the Franciscan Complex, Samana
837 Metamorphic Complex (Dominican Republic) and the Catalina Schist suggests that Li is mobile
838 in subduction-related metamorphic fluids, and provides a source of information about the history
839 of multiple fluid sources during metamorphism. Mafic blocks found in mélangé generally have
840 higher Li concentrations and lower $\delta^7\text{Li}$ than presumed MORB or altered MORB protoliths,
841 suggesting infiltration of fluids derived from Li-rich sedimentary sources. Retrograde reaction
842 zones surrounding blocks have higher $\delta^7\text{Li}$ compared to mafic blocks and in some cases have
843 lower and in others higher Li concentrations compared to mafic blocks, suggesting a later fluid,

whose source cannot be constrained by Li compositions (Penniston-Dorland et al., 2010; 2012a,b).

In some settings, there is evidence for REE and/or HFSE mobility. The metamorphosed mafic rocks of the Catalina Schist and the Shuksan Metamorphic Suite (Washington State, USA) exhibit enrichments in HFSE and REE in some garnet amphibolite blocks compared to others and in reaction rinds relative to associated mafic blocks (Sorensen and Grossman, 1993). These enrichments are associated with crystallization of accessory minerals such as epidote, rutile, and titanite at relatively high- T conditions (500-800°C, 0.7-1.4 GPa). Lawsonitites in the Alpine Corsica (France) are found as reaction rinds at the contacts between metamafic, serpentinite or ophicarbonates and enclosing metasedimentary rocks (Vitale Brovarone et al., 2014) at somewhat lower- T conditions (lawsonite-blueschist unit $T\sim 350$ -460°C, $P\sim 1.5$ -1.8 GPa, lawsonite-eclogite unit $T\sim 490$ -550°C, $P\sim 2.2$ -2.4 GPa). These rocks exhibit extreme (>1000% mass gain) enrichment in Ca and Sr along with significant (50-500% mass gain) enrichment in REE and loss of LILE such as K, Rb, Cs and Ba.

7.1.6. Likely importance of the transition from hydrous fluid to silicate melt

The element transport capabilities differ greatly for aqueous fluid and silicate melt (see Hermann et al., 2006; Kessel et al., 2005). The significance of supercritical fluid for transporting mass has remained uncertain due to uncertainty in the positions of the relevant second critical end points in various H₂O-rock systems (see the discussions by Manning, 2004; Zheng and Hermann, 2014). Nonetheless, the P - T conditions at the subduction interface beneath arcs (i.e., at depths of 80-120 km) are sufficiently high (>600 °C) that some H₂O-saturated partial melting can occur (particularly of metasedimentary rocks), presumably providing greater potential for mass transfer.

7.2. *Contrasting metasomatic behaviors: closed vs. open system*

There are two endmember metasomatic styles observed at/near the subduction interfaces based on investigations of HP metamorphic suites. In one endmember, more intact or coherent volumes of rocks (sedimentary, mafic, ultramafic) behave as relatively closed systems. This has been documented in a number of the Alpine eclogite localities (e.g., Monviso: Philippot and Selverstone, 1991; Nadeau et al., 1993; Rubatto and Hermann, 2003; Spandler et al., 2011; the Swiss Alps: Getty and Selverstone, 1994; Widmer and Thompson, 2001; Barnicoat and Cartwright, 1995; Cartwright and Barnicoat, 1999). For metasedimentary rocks, Bebout and Fogel (1992), Bebout et al. (1999), Bebout and Nakamura (2003), and Bebout et al. (2013) invoked relatively closed-system Rayleigh-like devolatilization behavior in larger volumes of metapelites and metacarbonates. Collins et al. (2015) argued for relatively closed-system behavior in exposures of deeply subducted W. Alps metabasalts and ophicarbonate away from major shear zones and containing few larger, through-going veins. Closed-system behavior was indicated by a lack of evidence for appreciable decarbonation, consistent with little or no infiltration of the rocks by H₂O-rich fluids. Also, in many of these rocks, carbonate $\delta^{18}\text{O}$ is consistent with closed-system exchange with more abundant silicate minerals.

In the other endmember, fluid flow is focused into shear zones (including *mélange* zones) and fracture networks, as suggested by greater abundances of metasomatic features in shear zone matrices, relative to more intact rocks, and isotopic homogenization observed in shear zone matrices and veins (Bebout, 1991a,b, 2014; Selverstone et al., 1991; Barnicoat and Cartwright, 1995; Spandler and Hermann, 2006; see the discussions of permeability in subduction channel settings by Zack and John, 2007; Ague, 2007, 2014; Kawano et al., 2011; Spandler et al., 2011; van der Straaten et al., 2012; Angiboust et al., 2014b). This relationship was demonstrated for the

Catalina Schist paleoaccretionary complex, using the O, C, H, and N isotope compositions of rocks from mélangé zones and mineralized fractures in comparison with compositions for metasedimentary and metamafic rocks away from these structural features (see **Fig. 9**). Carbonate dissolution and carbonate reduction recently documented by Galvez et al. (2013) and Ague and Nicolescu (2014; also see the discussion by Lazar et al., 2014) indicate localized larger fluid flux in zones of structural weakness (i.e., particularly high permeability), in these cases along veins and in a fold hinge.

7.3. Contrasting deformation behaviors: intact vs. highly deformed

Field-based studies of HP metamorphic suites point to some common themes in the structural/lithologic makeup of the subduction plate interface, and the various field studies likely sample differing parts of evolving subduction interfaces (see **Fig. 1**). At one end of the deformation spectrum, relatively intact or coherent volumes of identifiably metasedimentary, metabasaltic/metagabbroic, and meta-ultramafic rocks occur within or separated by shear zones. These larger, more intact bodies in some cases appear to be sheets/tabular in morphology. The scales of these features vary widely, from 10s of cms to kms (Bachmann et al., 2009; Angiboust et al., 2011a,b; Whitney et al., 2014), and can be seen fragmenting into smaller blocks that begin to acquire more spherical geometries. Some aspect of all metamorphic exposures can represent this endmember behavior: intact intraslab rocks (with veins, less-developed shear zones; e.g., Sivrihisar; Whitney et al., 2014), large intact bodies with intervening more highly-developed shear zones (e.g., Monviso; Angiboust et al., 2011a,b), smaller spherical-geometry blocks within expanses of sheared matrix (mélangé zones of the Catalina Schist, New Caledonia, Syros; Bebout and Barton, 1993, 2002; Breeding et al., 2004; Spandler et al., 2008; Miller et al., 2009), and intact volumes of variably disaggregated meta-peridotite believed to represent hanging-wall

(mantle wedge) rocks to varying degrees metasomatized by fluids emanating from a subducting slab and sediments (e.g., Cannaó et al., 2015). These exposures lead to depictions of the subduction interface as a zone developed between subducting lithosphere sections and hanging wall (peridotite or other lithologies, particularly at greater depths; see **Fig. 1**).

At the other end of the deformation spectrum are highly deformed zones with schistose matrix. These zones are commonly referred to as *mélange* zones and generally have a fine-grained matrix that is composed either of sedimentary particles, such as clay minerals or have a large ultramafic component (serpentinite or talc/chlorite schists). The matrix rocks can include large tracts of chlorite-, talc-, and amphibole-rich schists containing few other minerals (Bebout and Barton, 1989, 1993, 2002; Spandler et al., 2008; Miller et al., 2009; Marschall and Schumacher, 2012). Where studied, the isotopic compositions of these matrix rocks are relatively homogenized, at up to km-scales, seemingly reflecting extensive fluid-rock interaction at such scales. These matrices contain bodies of less deformed mafic, sedimentary, and ultramafic rocks. The blocks found within these matrices have varying geometries, are up to km-scale, and can preserve disparate *P-T* histories reflecting dynamics of incorporation and entrainment. The blocks can contain mineralized fracture networks (vein arrays), at least in some cases with isotopic compositions indicating communication with the fluids mobilized within the matrices (see Bebout, 1991a,b, 1997; Penniston-Dorland et al., 2012a).

7.4. It's a matter of scale

It is easy to imagine that the deformation, and related fluid and mass transfer, at the subduction interface is distributed across multiple km scales, consistent with geophysical observations regarding a low seismic velocity zone at tops of many subducting slabs (see **Section 1**). Exhumed *mélange* zones in some cases are kilometers wide, such as the amphibolite-grade

mélange unit in the Catalina Schist, within which tectonic blocks of mafic and ultramafic rock range in scale from meters to 100s of meters (Bebout and Barton, 2002). In other suites, it is likely that the scale of the tectonic blocks is sufficiently large that the identification of more deformed matrix is greatly complicated. In some localities, preferential weathering of the mélange matrices leads to preferential exposure of the tectonic blocks, with or without attached matrix (e.g., in the Franciscan Complex, Tiburon Peninsula exposure).

The subduction interface should be thought of as a km-scale zone over which the distribution of strain is quite heterogeneous, with interleaving of strongly deformed zones and domains experiencing little deformation — from this perspective, a mélange unit such as that mapped by Bebout and Barton (2002) could be thought of as representing one of these more highly deformed zones. In this spirit, we have incorporated observations from subduction-zone metamorphic suites in which a quite diverse set of lithologies has experienced juxtaposition. We emphasize the implications of the styles of deformation in these zones for the release and mobility of fluids and the related mass transfer that is focused in the more deformed parts of the section. In summary, many of the differences in conclusions regarding fluid and mass transfer reviewed here relate to the scales at which the key observations were made and to which part of an evolving subduction interface is being investigated (see **Fig. 1**).

7.5. Significance and impacts of interface fluid and mass transfer

At all depths along the subduction interface there is evidence for fluids, whether in the form of veins, metasomatic reaction zones, or as alteration of the isotopic composition of more highly deformed rocks. In this section, we argue for the significance of fluid and mass transfer along the subduction interface and describe its impacts on the structural and geochemical evolution of subduction zones.

7.5.1. Role of fluids and mass transfer for seismicity

At shallow depths (<40 km), the rocks display a variety of deformation features (e.g. veins, slickenfibers, pseudotachylytes, cataclastic zones) that may have been associated with significant seismicity (see Rowe et al., 2005, 2011; John and Schenk, 2006; Fagereng et al., 2011; Deseta et al., 2014; Fisher and Brantley, 2014; Angiboust et al., 2015). Evidence from crack-seal veins of the Kodiak Formation led to the conclusion that silica distribution may play a role in modulating the frequency of plate boundary instability (Fisher and Brantley, 2014). Relationships between brittle deformation structures (cataclasites, veins) and ductile deformation structures (mylonitic rocks) suggest switching between brittle and ductile behavior in Arosa (Bachmann et al., 2009) and the Dent Blanche Zone (Angiboust et al., 2015), and suggest variations in strain rates and fluid pressures which are thought to be related to seismic activity. These observations suggest a strong relationship between build up of fluid pressure, seismic failure, and migration of fluids (see Husen and Kissling, 2001; Saffer and Wallace, 2015).

The presence of weak, hydrous sheet silicate minerals and free fluids (and higher pore fluid pressure) is generally believed to decrease the strength of the interface (Wada et al., 2008, 2012; Abers et al., 2013), and some believe that fluids play a key role in episodic tremor and slip (ETS) events observed in some subduction zones (e.g., Cascadia, NW Japan; Peacock, 2009; Audet et al., 2009; Gombert et al., 2010; Peacock et al., 2011; Audet and Bürgmann, 2014). Recently, some have suggested that the redistribution of quartz by fluids could significantly affect elastic properties and play a role in modulating periodic events such as earthquakes or slow earthquakes (Fisher and Brantley, 2014; Audet and Bürgmann, 2014; see **Fig. 2**). For the Cascadia margin, Hyndman et al. (2015) suggested a relationship between silica additions to forearc crust and the positioning of the ETS zone.

7.5.2. *Rheology and deformation-enhanced fluid infiltration*

The highly deformed mélange units found in many subduction interface exposures preserve a mixture of a variety of materials that have significantly different rheology. These materials respond differently to strain, in many cases resulting in the localization of strain within weaker materials. Relatively weak materials that may act as lubricating layers within subduction zones include sedimentary rocks (at $P < 2$ GPa) and serpentinites (at $P < 3$ GPa, Guillot et al., 2009). Experimental results on the deformation behavior of antigorite suggest that it may have a relatively low viscosity during deformation at low temperatures characteristic of subduction zones ($P=0.85$ to 4 GPa, $T=200$ -625°C; Hilairiet et al., 2007; Chernak and Hirth, 2010). Other sheet silicates such as talc (Escartin et al., 2008) and muscovite (Mares and Kronenberg, 1993) also behave in a relatively weak fashion and can lead to strain localization. The finer-grained matrices of plate interface mélanges are commonly composed of these relatively weak materials. Strain localization has been proposed to explain different records of strain in coexisting rocks. For example, in the Erro Tobbio unit (Voltri massif, Western Alps) antigorite mylonites and cross-cutting en-echelon olivine veins (indicative of prograde metamorphism) both record top-to-the-NW kinematics consistent with deformation during subduction. Pre-Alpine peridotite bodies contained within the antigorite mylonites, on the other hand, record only minor evidence of Alpine deformation (Hermann et al., 2000). This difference between the peridotite bodies and the antigorite mylonites is explained by localization of strain within the weaker serpentinite (Hermann et al., 2000).

In this way, strain can be partitioned in mélange zones into regions that contain relatively weak material. At Monviso, strain localization occurred in shear zones at lithologic interfaces regardless of the strength of materials (Angiboust et al., 2011a,b). While ductile deformation

dominated within these shear zones local brittle deformation is documented by eclogite breccias and fractured garnets thought to be linked with subduction zone seismicity (Angiboust et al., 2011a,b, 2012). Evidence from localities such as the Catalina Schist (e.g. Bebout, 1997; Penniston-Dorland et al., 2012a) and the Sesia-Lanzo Zone (Babist et al., 2006; Konrad-Schmolke et al., 2011) suggests that enhanced permeability due to the highly foliated nature of the matrix focuses fluid flow into these relatively weak regions of high strain (see the discussion by Ague, 2014).

Numerical modeling of the behavior of materials in subduction zones indicates that zones or layers of mixed material can develop at the subduction interface. Flow of material within the subduction interface has been modeled by Cloos (1982), Cloos and Shreve (1988a, b), Gerya and Stöckhert (2002), and Gerya et al. (2002) and is thought to be a possible mechanism for the exhumation of HP rocks. The effective rheology of the material within the subduction interface and the relative densities of the materials control this movement and the rate of exhumation (Cloos, 1982; Gerya and Stöckhert, 2002; Gerya et al., 2002). Density contrasts contribute to relative buoyancy of some subduction-related materials and have been postulated to lead to exhumation (e.g., Hermann et al., 2000; discussion by Agard et al., 2009). Serpentinite has a relatively low density ($\leq 2.7 \text{ g/cm}^3$), which suggests it can behave in a buoyant fashion, similar to continental crust within subduction zones (Reynard, 2013). Gerya et al. (2002) demonstrated that the lower the effective viscosity of the matrix material, the greater the degree of chaotic distribution of materials within the subduction interface. These studies have also concluded that *mélange* likely has a Newtonian rheology (dissolution precipitation creep) and not a power law rheology (dislocation creep) in order for material to be exhumed efficiently (e.g., Stöckhert, 2002). The rheology of mixed materials was investigated by Grigull et al. (2012). This study

found that blocks compose a volume percent that typically ranges from 5 to 50% of the block-in-matrix terrain. The study further modeled the subduction interface as a suspension of spheres in a low viscosity ($\leq 10^{19}$ Pa s) matrix and found that the effect of spheres within this matrix on the overall viscosity of the matrix was relatively minor – it changed the overall viscosity by less than one order of magnitude (Grigull et al., 2012).

Fluids are known to play key roles in deformation and mass transfer in shear zones (e.g., Selverstone et al., 1991; Dipple and Ferry, 1992; Axen et al., 2001; Barnes et al., 2004; Keller et al., 2004; Goncalves et al., 2012). The interplay between fluid flow, the development of hydrous minerals, and enhanced deformation can lead over time to the channelization of fluid flow which in turn results in significant mass transfer within these zones of channelized fluid flow as is observed in many of the *mélange* zones described in this review.

7.5.3. Duration of fluid infiltration events

Regular variations in elemental abundances and isotopic compositions present in reaction zones, and consistent with diffusive transport, have previously been well documented for some elements, such as Li (Penniston-Dorland et al., 2010; John et al., 2012) and Mg (Pogge von Strandmann et al., 2015). In these studies, the scale of diffusive transfer yields information regarding the timescales of diffusion. Petrographic evidence for fluid-rock interaction is coupled with evidence for variation in whole-rock isotopic compositions along profiles at the scale of cm to m. Numerical models are fit to the profile data and use existing information about elemental and isotopic diffusivities to extract information about the duration of the diffusive event which in turn relates to the duration of the fluid-rock interaction. The results yield timescales on the order of 100 years or less, suggesting that fluid is traveling through the rocks in relatively short pulses or bursts.

7.5.4. *Connection with arc lava compositions (and the deeper mantle)*

The heating related to the transit of subducting slabs and overlying sediment and sheared rocks as they come in contact with hot, convecting mantle, and the resulting greater devolatilization of some of these rocks, should be a recipe for the mobility of fluid and dissolved material. To add to this, the fluids are expected at these conditions to be transitioning from hydrous fluids to silicate melts, greatly increasing their capacity to dissolve and transport mass (see Hermann et al., 2006; see Fig. 1 in Kessel et al., 2005). It is possible that the enhanced metasomatism possible at these depths and temperatures could lead to the various compositions of deep-mantle geochemical reservoirs that invoke subduction zone metamorphism as their source (see discussion by Bebout, 2007; Ryan and Chauvel, 2014).

The fluids and/or silicate melts released in subducting sections beneath arcs may disproportionately bear chemical/isotopic signatures of rocks in higher-permeability zones that channelize and interact with these fluids to a greater degree. Thus, if km-wide shear zones (akin to the *mélange* zones examined in field studies of HP rocks) exist along the subduction interface, the fluid flow focused along these zones should exert a strong influence on the composition of the slab signature being delivered to the subarc mantle wedge. Likewise, if these fluids are mobilized along fracture networks developed in more coherent parts of the subducting section (i.e., the zones showing more brittle deformation), they would tend to inherit chemical compositions related to exchange with host-rocks along fracture surfaces.

In general, the evidence for element mobility along the deep-forearc subduction interface is compatible with the compositions of fluids entering the mantle wedge and contributing to arc magma generation (e.g., the “IRS fluids” of Gill, 1980). As has been discussed previously by Bebout and Barton (2002), King et al. (2006, 2007), Spandler et al. (2008), and Marschall and

Schumacher (2012), fluids emanating from slab sections and interacting with *mélange*-like zones would be expected to acquire “hybrid” signatures related to this mixing in these zones (see **Figs. 18, 19**). It is possible that fluids bearing these signatures could simultaneously satisfy the various mixing endmember criteria derived from the study of arc volcanic rocks. King et al. (2006) noted such hybrid signatures in individual hand samples of the Catalina Schist amphibolite-grade *mélange* matrix. There, rocks that appear to represent endmember ultramafic compositions (e.g., an ultramafic chlorite-anthophyllite schist with low SiO₂ (41.3 wt. %) and high MgO (28.6 wt.%) and low alkalis) preserve Sr and Nd isotope ratios indicative of a more evolved rock (e.g., $^{87}\text{Sr}/^{86}\text{Sr} = 0.70590$, $\epsilon\text{Nd} = -3.30$). King et al. (2006) noted that it could be difficult to discern whether contributions from various rock types calculated from arc volcanic data represent proportions of distinctly separate parts of the pre-subduction section, or if they reflect the signature of a hybridized rock. *Mélange* matrix samples from the various units of the Catalina Schist, many of them now ultramafic or chlorite-rich schists, likely bear Pb isotope compositions of the sediments subducted into this paleomargin, mixed to varying degrees with mafic compositions (**Fig. 18**; King et al., 2007). Those authors argued that arc volcanic rocks could bear signatures of mixture between a hybridized *mélange* component and an upper mantle source. Marschall and Schumacher (2012) similarly argued that *mélange* rocks carry much of the geochemical signature of arc volcanic rocks and that devolatilization and melting of such rocks, as they rise in diapirs in the mantle wedge, could deliver this signature to arc source regions (see **Fig. 19**).

The fluid and mass transfer along structurally complex subduction interfaces can result in significant metasomatic alteration of rocks conveyed to depths beyond those beneath magmatic arcs. The metasomatism and transit of these rocks to great depths in the mantle could lead to the

production of some of the chemically/isotopically distinct reservoirs invoked in studies of ocean island basalts (Hofmann, 2014; Ryan and Chauvel, 2014; also see Brenan et al., 1995). Bebout (2007) discussed the general lack of evidence in exhumed subduction-related metamorphic rocks for the fairly massive element losses (e.g., for Pb and U relative to Th) invoked to generate the geochemical characteristics of mantle reservoirs such as HIMU, EM1, and EM2 (Zindler and Hart, 1986; Hoffman, 2014) and suggested that losses of this magnitude could be achieved at greater depths beneath arcs that are not represented in the HP/UHP metamorphic suites (i.e., at subarc depths and beyond). We suggest that deformation-enhanced fluid infiltration and related mass transfer at depths >80 km, where the interface experiences temperatures >600 °C (see the *P-T* paths in **Fig. 4**), could contribute to greater element loss and possibly lead to residues with compositions corresponding to these reservoirs.

7.5.5. Stabilization of hydrous mineral assemblages and importance for volatiles cycling

Fluid-rock interactions at the interface in many cases result in the production of hydrous, nearly mono-mineralic rocks (e.g., chlorite-talc schists) that can stabilize a hydrous component to great depths in subduction zones (Bebout and Barton, 2002; Spandler et al., 2008; Miller et al., 2009; Marschall and Schumacher, 2012). In general, hydrous phases such as chlorite and talc have far greater *P-T* stability when they are essentially the only phase present in a rock than they have when in rocks containing multiple phases (e.g., subducting sediments and basalts). As noted by Bebout (1991a), chlorite in subducting basaltic and sedimentary rocks would be expected to break down at shallower depths than chlorite in hybrid rocks such as *mélange* matrix, with breakdown conditions also depending on the *P-T* paths they experience, which in turn are related to the dynamics of the subduction margin. The depth of breakdown of these hydrous minerals will determine the cycling of H₂O during subduction (see the study of chlorite stability by Lakey

and Hermann, 2015), thus the presence of hybrid rocks will stabilize H₂O to greater depths and lead to greater amounts of H₂O subducted deep into the mantle.

7.5.6. Deformation-enhanced decarbonation and carbonate dissolution

Recent work by Cook-Kollars et al. (2014) and Collins et al. (2015) is a reminder that carbonate-bearing rocks often require infiltration by low- X_{CO_2} fluids in order to drive extensive decarbonation reactions. Cook-Kollars et al. (2014) demonstrated that, without such infiltration, much or all of the carbonate in the Schistes Lustres/Cignana metasedimentary suite would have been retained to depths of up to 90 km approaching those beneath many volcanic fronts. This relationship is demonstrated in **Fig. 20A**, which shows contours of concentrations in volatiles CO₂ and H₂O calculated for closed-system devolatilization behavior for a hydrated and carbonated basaltic composition (from ODP Site 417/418). For this closed-system scenario, the basalts largely retain their CO₂ to depths of 90 km. However, as is shown for the same basaltic composition in **Fig. 20B**, infiltration by extremely H₂O-rich fluids, perhaps in part from dehydrating sub-crustal ultramafic rocks in slabs, can drive large amounts of decarbonation at relatively low temperatures (<500 °C). Theoretical calculations of carbonate solubility suggest that fluids released from dehydration of serpentinites at the base of the subducting slab could dissolve additional C in transit upward toward the plate interface (Kelemen and Manning, 2015; **Fig. 21**). Fluids could then enter the mantle wedge, contributing to forearc and subarc C storage in ultramafic rocks or addition of C to arc magmas, or they could be transported up-dip along the subduction interface, in some cases (depending on the P - T path they experience, see for example path 1 in **Fig. 17**) leading to precipitation of C in minerals. The abundant carbonate veins in many forearc metamorphic suites could reflect this up-dip fluid transport and related precipitation (see the contours of [C] in ppm in **Fig. 21**, from Kelemen and Manning, 2015).

Another important factor is the tendency of mixed carbonate-silicate compositions to undergo more dramatic decarbonation than more pure carbonate rocks, related to the need for silicates in order for carbonates to react and decarbonate. In one extreme, a 100% carbonate rock could be subducted to extreme depths in the upper mantle before experiencing decarbonation to produce CaO and CO₂. Presumably, access of fluids to subducting rocks with evolving permeability (Ord and Oliver, 1997), is also necessary to facilitate the carbonate dissolution and redox-related C loss recently documented by Ague and Nicolescu (2014) and Galvez et al. (2013). The mixing that occurs in shear/mélange zones can juxtapose carbonate-rich and carbonate-poor rock types, in a fluid-rich environment, leading to metasomatic exchange and resulting reactions in some cases involving decarbonation. Thus, processes of the type demonstrated for these zones of mixing could greatly enhance loss of CO₂, particularly beneath deep forearcs and subarcs, conceivably releasing sufficient CO₂ to balance with the arc volcanic CO₂ output (see the discussion by Collins et al., 2015). The extent to which this occurs could depend on the unknown amounts of H₂O-rich fluid released from sub-crustal ultramafic rocks in subducting slabs. This H₂O-rich fluid could rise from hydrated oceanic lithospheric mantle into the subduction interface and be focused in shear zones and more highly fractured rock volumes to react with the hybrid rocks within the interface.

8. Conclusions and Future Directions

One commonality in virtually all studies of HP metamorphic rocks is the abundant evidence for the presence of a free fluid phase and heterogeneity in the availability and transport of fluid as related to structural setting. At the shallowest levels, pore fluids contribute significantly, mixing with fluids generated by diagenetic and metamorphic reactions. At greater depths, fluids

are generated by devolatilization reactions. At all depths studied and considered in this review, fluid flow is focused along fractures and in shear zones, likely with a far smaller degree of pervasive fluid transfer. The heterogeneous deformation that occurs along subduction interfaces in general leads to focusing of fluid flow along the more highly deformed regions.

The exact fluid loss profiles, for subducting lithologies along subduction interfaces, likely vary as functions of the rock types and thermal structure of the margin, the latter dictating the prograde P - T paths the rocks experience. These differences in thermal structure will also affect the element/mineral solubilities along the subduction interface, and thus the mass transfer that occurs. A number of recent studies of forearc devolatilization appear to document the retention of large fractions of the initially subducted volatiles content of several important rock types. However, these studies have in general been focused on consideration of devolatilization in more intact volumes of these rock types, not in more highly deformed zones (shear zones and more highly fractured volumes) where disparate rock types can be structurally juxtaposed and through which flow of externally-derived fluid can be focused. Devolatilization, and related mass transfer, can in general be enhanced along subduction interfaces, particularly if loss of large amounts of H_2O -rich fluid from sub-crustal ultramafic rocks in slabs results in flushing of the overlying interface.

Studies of the subduction interface have been restricted to exposures representing forearc depths, due to the general lack of suitable exposures representing the greater depths beneath magmatic arcs (i.e., >100 km). We suggest that the fluid processes beneath arcs could lead to far more extensive mass transfer and related metasomatism of the subducting section and overlying mantle wedge, enhanced by the higher temperatures and the transition of the dominant fluid type from hydrous fluid to silicate melt. Beneath most arcs, subduction interfaces experience

temperatures of $>600^{\circ}\text{C}$, approaching the temperatures of the wet solidi for relevant rock compositions, and in general resulting in far higher solubilities of elements of interest in studies of surface-to-mantle chemical cycling.

We suggest some research directions that will likely be fruitful in shedding light on the nature of the subduction interface and attendant fluid and mass transfer.

— Some extremely important questions remain regarding large-scale chemical cycling of elements and compounds, particularly volatiles, and the roles of interface deformation and fluid processes in this cycling. Significant effort has been directed towards the understanding of the cycling of H_2O , and future work should focus on understanding the other elements forming major volatile species (C, N, and S). Other geochemical indicators such as those that have the potential to shed light on fluid flow within subduction zones include fluid-mobile elements such as B and Li and the halogens.

— The roles played by deformation and rheology in fluid flow and mass transfer are still relatively poorly understood. Future work should include studies aimed at shedding light on the relationship between deformation and mass transfer.

— The work to date has demonstrated a number of ways in which fluids are related to patterns of seismicity. Evidence for relatively short durations of fluid flow events suggests a more episodic nature of fluid flow during subduction metamorphism. Further attention should be paid to understand the periodicity of such flow and its relationship to seismicity.

— Quantitative estimation of fluid fluxes based on evidence from subduction-related metamorphic rocks remains a somewhat elusive goal. In many cases, the spatial constraints necessary for this evaluation are missing. Further evaluation of fluid fluxes during subduction metamorphism, using the most recent thermodynamic modeling results (e.g., Dolejs and

Manning, 2010; Sverjensky et al., 2015), would shed further light on the quantities of fluids traveling through metamorphic rocks during subduction zone metamorphism.

— For a comprehensive understanding of subduction zones, observations and analyses of samples collected in the field, such as those presented here, need to be integrated with experimental work and thermodynamic and geodynamic modeling. Sample collection and the analytical strategies chosen need to be informed by questions raised by geodynamic models. The results of geodynamic models in turn need to be evaluated by comparisons with evidence from natural samples (e.g., Penniston-Dorland et al., 2015). Interpretations of fluid fluxes and fluid sources have a more quantitative basis when thermodynamic modeling and experimental constraints are considered.

— Geophysical observations should also be used to directly test petrologic models. Intriguing suggestions that *mélange* lithologies along the interface become gravitationally unstable and rise diapirically into the mantle wedge, conveying volatiles and transferring geochemical signatures of the interface into arc magma source regions (see Gerya and Yuen, 2003; Behn et al., 2011; Marschall and Schumacher, 2012) could potentially be tested through geophysical observations.

— Further investigation of rocks from the subduction interface should be focused on the amounts of fluid contributed to subduction interfaces from dehydrating ultramafic rocks in the sub-crustal mantle of subducting slabs. Massive flushing of the interface by this fluid could have profound implications for fluid and mass transfer, including C release, at depth along the interface.

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Figure Captions

Figure 1. Sketch of ocean-continent subduction zone, showing key structural elements and scenarios for the nature of the plate interface at shallow and deeper levels. The two boxes show general structural styles and indicate schematically some likely fluid flow geometries and are based on the published field studies of units described in this paper. Diagram is not to scale.

Figure 2. Conceptual model of how silica enrichment controls slow earthquake behavior in northern Cascadia (from Audet and Bürgmann, 2014; also see Fisher and Brantley, 2014). k = permeability; σ_e = normal effective stress. Low ratios of compressional (P)-wave velocities to shear (S)-wave velocities (v_p/v_s) measured in the forearc crust are interpreted to reflect forearc silica enrichment. Following a slow-slip event permeability increases, allowing fluid circulation, silica precipitation, and a reduction in pore-fluid pressure. The strong temperature-dependence of silica solubility results in higher permeability reduction in quartz gouge, faster re-sealing and overpressure development (shown here as decreasing effective normal stress), and thus lower recurrence times with increasing temperature. Thin dashed lines are 200°C isotherms.

Figure 3. Connection of field observations of the metamorphic rock record in (A), a section across the Dent Blanche Thrust (DBT, Swiss Alps) showing the geometry of Arolla gneisses (underplated continental crustal slices) and underlying ophiolite (Ollomont area; Angiboust et al., 2014a) with large-scale coupling/decoupling at the subduction interface in (B), a view of the subduction interface, and relationships with seismic coupling, based on field study of the DBT (Angiboust et al., 2015). Inset shows deformation features associated with partially coupled transition zone.

Figure 4. Peak-metamorphism P - T estimates for the subduction interface suites discussed in this paper superimposed on P - T paths calculated by Gerya et al. (2002; red lines) and Syracuse et al. (2010, updated van Keken pers. comm., 2014; green lines) by region. The model average for Syracuse et al. (2010) is shown as a thicker green line. The thick red line represents “Model A” of Gerya et al. (2002). A global mean distribution of rock-based P - T estimates (at P_{max}) from Penniston-Dorland et al. (2015) is shown as the dark blue curve with a paler blue $\pm 2\sigma$ confidence envelope. Model P - T predictions in general match the rock P - T estimates well for $P > 2.5$ GPa; however, at shallower depths (< 2 GPa), the P - T estimates from metamorphic rocks are for a given pressure, hotter than the P - T predictions of both models. The rock-based average is hotter than Model A of Gerya et al. (2002) by ~ 100 °C and hotter than the Syracuse et al. (2010) average by more than 200 °C. The peak metamorphic P - T conditions of units discussed in this paper are outlined by rectangles (see **Table 1**), and the boundaries between the

blueschist and eclogite facies (figure modified after Penniston-Dorland et al., 2015) and the boundary of the “Forbidden Zone” (from Liou et al., 2000) are shown as gray lines.

Figure 5. (A) Macroscopic schematic cross section through the subduction mélange and the Austroalpine upper plate at the Arosa locality, Switzerland. (B) Interpretative three-dimensional cross-section of a forearc region illustrating interface deformation and veining and inferred stable and unstable regions (both figures are from Bachmann et al., 2009).

Figure 6. Schematic diagrams showing the tectonic setting of the Mugi mélange and the varied geological occurrences of syn-tectonic veins (from Yamaguchi et al., 2012, and references therein). (A) Schematic profile of the Nankai Trough, as derived from seismic profiles, showing the position of the seismogenic zone. (B) Illustration of the structural and tectonic setting of the Mugi mélange. (C) Schematic block diagram showing the geological occurrences of four types of veins that were identified by Yamaguchi et al. (2012), and their relationships with the mélange and ramp thrust of the duplex structure. Veins are widely developed within the basaltic rocks. Boudin-neck veins are observed at the neck regions of pinch-and-swell and boudinage structures in the mélange. Network veins are developed in damage zones along the ramp thrust, and fault-fill veins occur along dilational jogs in the thrust.

Figure 7. Peak metamorphic temperature vs. calculated (A) $\delta^{18}\text{O}$ and (B) $\delta^{13}\text{C}$ for CH_4 -bearing H_2O -rich fluids equilibrated with carbonate-bearing veins in various units of the Franciscan Complex and lawsonite albite (LA) and lawsonite blueschist (LB) units of the Catalina Schist rocks (from Sadofsky and Bebout, 2001, 2004). Small black diamonds indicate the isotopic compositions of the veins, and shaded rectangles indicate calculated fluid $\delta^{18}\text{O}$ based on the $\delta^{18}\text{O}$ of the vein carbonate. The black curve in (A) indicates fluid $\delta^{18}\text{O}$ calculated for quartz with $\delta^{18}\text{O}_{\text{VSMOW}} = +19\text{‰}$ (curved line). Match between this curve and fluid compositions calculated from vein $\delta^{18}\text{O}$ values (gray-shaded boxes) suggests some buffering of fluid isotopic composition by the host rocks. However, host rock quartz $\delta^{18}\text{O}$ ranges from +12 to +19‰, thus the vein $\delta^{18}\text{O}$ values are not uniformly equilibrated with the host rocks, perhaps consistent with some influence of externally derived fluids and/or the homogenization of fluid isotopic compositions through mixing of fluids equilibrated with sediments having a range of $\delta^{18}\text{O}$. The region “Decollement Fluids” indicates the $\delta^{18}\text{O}$ of H_2O sampled from fault zones in active accretionary prisms (e.g., Kastner et al., 1991). (B) Plot showing that $\delta^{13}\text{C}_{\text{VPDB}}$ values calculated for CH_4 in equilibrium with the calcite veins are in isotopic equilibrium with reduced C (metamorphosed organic matter) in the host rocks. (C) Field photograph of a typical exposure of metasedimentary rock, in the lawsonite-albite-facies unit of the Catalina Schist, containing multiple generations of calcite+quartz veins. Such veining is also observed in the Franciscan Complex (see Sadofsky and Bebout, 2001, 2004; horizontal dimension of ~1m).

Figure 8. Major element concentrations (in wt.%) for mafic and ultramafic blocks, reaction rinds, and samples of mélangé matrix demonstrating that the mélangé matrix compositions can be explained by mixing of mafic and ultramafic rocks, but with the necessity of significant addition of SiO₂. Stable isotope compositions of the mélangé matrix are consistent with infiltration of H₂O-rich fluid previously equilibrated at somewhat lower temperatures with metasedimentary rocks (Bebout and Barton, 1989; see **Figs. 9A,B**). These fluids could also have delivered Si to the subduction interface along which this mélangé unit was developed (Bebout and Barton, 1993).

Figure 9. (A) Calculated O isotope compositions of H₂O in equilibrium with metasomatized rocks from shear zones and fractures and some less altered rocks (from Bebout and Barton, 1989). In the highest-grade unit (amphibolite), large expanses of relatively intact metabasaltic and metasedimentary rocks preserve $\delta^{18}\text{O}$ out of isotopic equilibrium with the fluids with $\delta^{18}\text{O} = +13 \pm 1\text{‰}$ (gray-shaded band) that preferentially infiltrated shear zones and highly fractured domains on a regional scale (also see Bebout, 1991a). **(B)** $\delta^{18}\text{O}$ of calcite from relatively undeformed expanses of lawsonite-albite (darker-shaded) and lawsonite-blueschist (lighter-shaded) metasedimentary rock compared with values for calcite in veins and in mélangé matrix (from Bebout, 1991b). As in **B**, the vertical gray-shaded band shows the uniform isotopic composition of the vein-forming fluids with which the calcite in veins and mélangé matrix are more extensively equilibrated ($\delta^{18}\text{O} = 13 \pm 1\text{‰}$; $\Delta^{18}\text{O}_{\text{calcite-water}}$ for the relevant temperatures is in the range of +2.0 to +4.0‰; see Bebout, 1991b). The field photographs are of lawsonite-blueschist mélangé matrix **(C)**; horizontal dimension is ~30 cm) and amphibolite mélangé matrix **(D)**; hat for scale).

Figure 10. Block-matrix relationships in the lawsonite-blueschist mélangé unit of the Catalina Schist. **(A)** Field photo of mafic block core, rind and matrix. **(B and C)** Closeup (photograph and sketch) of region in white box in **A** showing complex interface between block rind and matrix. **(D)** A comparison of the geochemistry of block rinds with block cores demonstrating rind enrichment (higher concentrations) in elements associated with ultramafic rocks, variable concentrations of elements generally considered fluid mobile, and rind depletion (lower concentrations) in elements associated with mafic rocks relative to block cores. **(E)** Os concentrations and isotope compositions consistent with simple mixing (mixing curves shown) of mafic and ultramafic components (from Penniston-Dorland et al., 2014).

Figure 11. (A) Field relations in shear zones in New Caledonia (from Spandler et al., 2008). Highly deformed matrix in shear zones between larger volumes of intact mafic rocks and containing smaller blocks of mafic, sedimentary, and ultramafic rocks. Sheared matrix is either chlorite- or talc-rich. **(B and C)** Trace element compositions of mafic and ultramafic, and hybridized, rocks in the shear zone, normalized to chondrite. **(B)** Compositions of talc schist sample 2814, talc-amphibole schist sample 1015, chlorite schist sample 2816, and serpentinites (various open symbols). The field for associated

mafic rocks is shown as the dark grey field (data from Spandler et al. 2004a). (C) Serpentinite (gray field) and talc schists.

Figure 12. Mineralogy and major and trace element concentrations across a Tianshan vein envelope developed in an intraslab fracture network (from Beinlich et al., 2010). (A) Variation in mineral modes, (B) Variation in major element concentrations, (C) Loss of some elements adjacent to the vein (Li, Cs, Rb, Ba, K₂O), and (D) Metasomatic addition of some elements (CaO, Sr, Pb). Shown in (E) is a field photograph of the vein, the eclogitic selvage, the transition zone, and the host-rock blueschist (from Beinlich et al., 2010; also see the study of the same traverse by John et al., 2012).

Figure 13. Evidence for fluid-mediated metasomatic exchange between mélangé matrix and metasedimentary rocks in the Syros mélangé unit (from Breeding et al., 2004). (A) Sketch of blocks in matrix and reaction zone adjacent to matrix, and (B) Geochemical data demonstrating that in the metasedimentary rocks, the destabilization of phengite resulted in large depletions in K, Rb, Cs and Ba.

Figure 14. Evidence for the dissolution of carbonate in high-*P* metamorphic rocks exposed on Syros and Tinor (from Ague and Nicolescu, 2014). (A) Field photograph of unaltered carbonate on right, green altered carbonate on left, (B) Field photograph of glaucophane (gl)-epidote (ep) rich alteration zone in carbonate rock adjacent to quartz (q) vein, (C) Field photograph of epidote-quartz vein surrounded by omphacite (om)-rich alteration zone, (D) Photograph of omphacite and glaucophane rich alteration zone adjacent to vein. (E and F) Proposed tectonic settings for carbonate dissolution in these exposures, also from Ague and Nicolescu (2014), on Syros (E) and Tinos (F). This dissolution in underplated carbonate-bearing rocks could be facilitated by infiltration of fluids from evolving major shear zones (mélangé zones) acting as fluid channelways (also see Breeding et al., 2004; Fig. 13).

Figure 15. Field relations, geochemistry, and tectonic setting of an intraslab shear zone exposed at Monviso, NW Italy (from Angiboust et al., 2014b). Fluid-rock interaction resulted in additions of the LILE Rb and Ba and elements sourced in the ultramafic shear zone matrix (Cr and Ni). (A) Field relations at/near the brecciated margin of a metabasaltic block in this shear zone. (B) Zoning anomalies, including Cr zoning, in garnets growing in the progressively metasomatizing blocks indicating possible mobility of these elements in metamorphic fluids. (C) Subduction interface setting for this shear zone and structural relationships at Monviso, where intraslab shear zones at/near the interface are developed between large zones/sheets of intact mafic eclogite showing different peak *P-T* history (from Angiboust et al., 2014b). The LSZ (Lower Shear Zone) contains smaller, more spherical mafic blocks with metasomatic rinds and brecciation at their rims (Angiboust et al., 2012). Fluid mobility, indicated by blue arrows, was concentrated in the shear zone and in fractures in mafic blocks showing brittle deformation behavior.

Figure 16. Views of the subduction interface from Spandler et al. (2008) and Cannaò et al. (2015) emphasizing the development of *mélange* and the importance of the dehydration of chlorite, antigorite, and talc for the fluid and mass transfer in this region. **(A)** Schematic model of interaction between different geochemical reservoirs at the plate interface environment and main geochemical implications (from Cannaò et al., 2015; redrawn after Trommsdorff, 1990). **a)** Release of H₂O-rich fluids sourced from *mélange* and dehydration of *mélange* serpentinites and of serpentized wedge, could trigger arc magmatism and explain the geochemical anomalies characteristic of many arc lavas; **b)** Geochemical anomalies introduced into arc magma source by ascent of serpentized wedge diapirs due to their low density compared to the surrounding materials and their “spongy behavior” for sedimentary-like elements and isotopes (from Cannaò et al., 2015). **(B)** One model for the devolatilization and partial melting resulting in arc magmatism, invoking the presence of a hybridized zone at the interface that is partially melted, yielding hybrid-slab chemical signatures (from Spandler and Pirard, 2013).

Figure 17. Quartz solubility as a function of *P* and *T*, plotted as contours of dissolved silica (contours of log molality of aqueous SiO₂ in equilibrium with quartz, from Manning 1994), and generalized “fluid” *P-T* flow trajectories that can be envisioned in a slab-mantle interface environment (see text for discussion; also see Bebout and Barton 1993; Bebout, 2013). The inset shows the possible geometry of fluids experiencing *P-T* Paths 1 (blue) and 2 (green) on this diagram, Path 1 up-dip along the interface and Path 2 initially up-T within the slab toward the interface, then down-T during up-dip transport similar to that experienced along Path 1. A critical end point on the hydrous melting curve of quartz lies at 1,080 °C and 9.5–10 kbar (Newton and Manning 2008).

Figure 18. Compositions of “hybrid” rocks developed in *mélange* zones for Pb isotopes compared with representative arc volcanic compositions (from King et al., 2007). The data for the Izu arc volcanic rocks, and subducting sediment and altered oceanic crust (AOC) are from Hauff et al. (2003). The average composition of the Izu volcanic rocks (star) has been explained as representing a mixture of an AOC component (90%) and a sediment component (10%; see the black, nearly vertical line indicating this mixing), whereas this composition could alternatively be produced by a mixture of a hybridized mafic-sedimentary-ultramafic *mélange* component with the composition of the mantle source (see the red line). NHRL = Northern Hemisphere Reference Line (after Hart, 1984).

Figure 19. Trace element compositions of “hybrid” rocks developed in *mélange* zones (open circles in **A** and **C**, black line in **B**), compared with arc volcanic rock compositions (from Marschall and Schumacher, 2012). These authors argued that there is great overlap in the overall geochemical characteristics of *mélange* rocks with the compositions of arc volcanic rocks. Thus, as was also suggested by Bebout and Barton (2002) and King et al. (2006, 2007), partial melting of a previously

hybridized lithology (mélange) could deliver the apparent mixture of sediment, AOC, and upper mantle proposed for arc magmas.

Figure 20. Demonstration of the enhanced decarbonation that can occur at the subduction interface due to infiltration of carbonate-bearing rocks by extremely H₂O-rich fluids (from Collins et al., 2015). **(A)** *P-T* diagram showing calculated volatiles concentrations for a ODP Site 417/418 altered oceanic crustal composition from Staudigel et al. (1996), for a closed system scenario (i.e., no infiltration by H₂O-rich fluids), and recently published prograde *P-T* paths for sediment cover on subducting slabs (T=Tonga, NV=N. Vanuatu, N=Nankai, C=Cascadia) from Syracuse et al. (2010; also van Keken et al., 2011, P. van Keken, pers. comm., 2013). Contours are the H₂O and CO₂ concentrations of this rock composition and the shaded rectangles are peak *P-T* of the metabasaltic units studied by Collins et al. (2015). The large brown-shaded arrow indicates the expected *P-T* trajectory taken at ~80-120 km depths by rocks subducting into most modern margins, involving heating to >600 °C related to exposure of the slab to the convecting mantle wedge (see Syracuse et al., 2010). **(B)** T-XCO₂ diagram for the same basaltic composition for ODP Sites 417/418 (from Collins et al., 2015), showing mineral stabilities at 2.5 GPa as a function of T-XCO₂. Reactions releasing CO₂ occur at lower *T* when fluid composition is H₂O-rich, leading to significant progress of decarbonation reactions when rocks are infiltrated by H₂O-rich fluids. **Panels 1-2** in the lower part of **(B)** detail the modal abundance changes that would occur, according to relationships in the T-XCO₂ diagram above, during the infiltration of this rock by an extremely H₂O-rich fluid, at two different temperatures at 2.5 GPa (the two dashed arrows in the middle diagram; see the discussion by Collins et al., 2015). Note the complete disappearance of carbonate in both scenarios when rocks are infiltrated by extremely low-XCO₂ fluids. Without infiltration by these H₂O-rich fluids, this rock would require heating to >600 °C for significant loss of CO₂ by decarbonation, as is shown in **(A)**.

Figure 21. Demonstration of the CaCO₃ solubility in aqueous fluids and the possible dissolution that could occur at/near the subduction interface (from Kelemen and Manning, 2015). **(A)** Pressure-temperature diagram showing contours of [C] (C concentration) in parts per million for aqueous fluids saturated in CaCO₃. Overlain are the *P-T* paths modeled for several modern subduction margins (from Syracuse et al., 2010). Dashed lines represent the paths for the base of the subducting oceanic crust and the solid lines are the paths for the top of the volcanics and sediments (i.e., at the subduction interface). The solid grey curve is the stability limit of serpentine (from Ulmer and Trommsdorff, 1995). **(B)** Figure similar to that in **(A)** but showing only the Aleutian *P-T* paths. The upper arrow represents the *P-T* trajectory that would be taken by fluids generated by dehydration of serpentine in the upper mantle of the subducting slab. C solubility increases along this path. The lower arrow shows a trajectory that

2047 could be taken by fluids exsolved from melts rising into the mantle lithosphere and crust of the
2048 overlying plate. The degree to which flushing of fluids derived from dehydrating sub-crustal ultramafic
2049 sections occurs within the subduction interface is a key open question in considering the fluid-rock
2050 evolution of the subduction interface.

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Table 1. Summary information about HP metamorphic suites

Locality	Age (Ma)	P (GPa)	T (°C)	Rock types	Matrix compositions	Features
Arosa	~60-35 (lower plate)	0.2-0.7	150-350	pelagic chert, metabasalt, metagabbro, serpentinite, turbidite (lower plate origin) metamorphic basement, dolomite (upper plate origin)	shale, serpentinite	Blocks in matrix, pseudotachylytes, veins, dip angle of 8°
Shimanto Belt - coherent <i>Hiwasa</i> Formation - <i>Mugi</i> mélange	Tertiary	0.1-0.2 (Mugi)	150-255 (Mugi)	<i>Hiwasa</i> mostly terrigenous turbidites. <i>Mugi</i> mélange include basalts, pelagic cherts, red shales, hemipelagic shales in black, scaly shale matrix	Black, scaly shale matrix	Sandstone and tuff blocks in scaly shale matrix. Pseudotachylyte and ultracataclasites Quartz veins
Chichibu Belt	Jurassic	0.5-0.6	230-290	psammitic and pelitic rocks, chert, greenstones, limestones	Pelitic schist	Mélange, veins
Kodiak Complex <i>Uyak</i> <i>Kodiak</i> <i>Ghost Rocks</i>	< 55	0.2-0.4	200-300	<i>Uyak</i> – mélange with greenstone, graywacke, gabbro, ultramafic blocks in chert-argillite matrix <i>Kodiak</i> – thin-bedded turbidites and massive sandstone only locally disrupted <i>Ghost Rocks</i> – mélange with sandstone, shale and pillow basalt	chert-argillite	Blocks in matrix, crack-seal veins pseudotachylite, cataclasite
Franciscan Complex - <i>Blueschist blocks</i> - <i>Eclogite blocks</i> - <i>Intact Metasedimentary</i>	140-170	0.5-0.6 2.0-2.5 0.2-0.8	300-350 550-620 ~200	Blueschist, eclogite, garnet amphibolite, metagraywacke, chert	Shale, serpentinite	Veins, blocks in matrix, reaction zones around mafic blocks

Catalina Schist	~115 to 95	0.6-1.2	~200-700	Metasedimentary (including metaconglomerate), metamafic, and metaultramafic rocks	Amphibolite facies matrix in places is chlorite schist and in places amphibole-, talc-schist	Veins, mélange blocks in matrix, reaction zones around mafic and ultramafic blocks, metasomatically altered igneous cobbles in metaconglomerates
Mount Hochwart - <i>Metasomatic conditions</i>	330	< 1.2	660-700	Garnet-spinel peridotite lenses within garnet-kyanite gneiss of the Ulten Zone	Garnet-kyanite gneiss	Variable thickness metasomatic bands at contact between peridotite and felsic gneiss
Dent Blanche Thrust - <i>Arolla gneiss</i> - <i>Tsaté Complex</i>	43-48 37-42	1.2 1.0-1.2	~450 360-490	Gneiss Calcschists, metagabbro pods in serpentinite	serpentinite	Serpentinite thrust zone containing metagabbro blocks in serpentinite, cataclastic layers containing quartz-epidote veins
Sesia Zone	Cretaceous-Tertiary	1.0-2.0	500-600	Continental lithologies – pelitic, calcareous pelitic, metagranitoids, metabasites, carbonates, quartz-rich rocks		Relatively weakly deformed Mombarone Unit separated from other units by blueschist-facies mylonitic shear zone
New Caledonia - <i>Diahot Blueschists</i> - <i>Pouebo Eclogite Mélange</i>	Eocene	1.6-1.9	550-600	<i>Diahot Blueschists</i> – thick sequence of metamorphosed blueschist sedimentary rocks with intercalated basalts and rhyolites <i>Pouebo Eclogite Mélange</i> – eclogite, garnet blueschist, garnet amphibolite, metamorphosed ultramafic rocks, quartz-garnet-mica schists	Talc-chlorite-phengite-quartz-amphibole matrix	Blocks in matrix, reaction zones rich in chlorite and talc
Tianshan HP	343-346	1.8-2.3	480-580	Metasedimentary rocks, including marble, metamafic	Blueschist metasedimentary	Veins, reaction zones around veins, blocks in matrix, fluid

				and metaultramafic rocks	matrix – felsic pelitic schist	inclusions
Syros and Tinos	Cretaceous-Eocene	1.3-2.0	470-520	Eclogites, blueschists, metagabbros, serpentinites, metaplagiogrinites, metasedimentary rocks	Serpentinite, metasedimentary	Reaction zones developed at contacts between mafic blocks, metasedimentary rocks, and/or serpentinite.
Erro-Tobbio and Voltri - <i>peridotite</i> - <i>eclogite</i>	Alpine	2-2.5 1.3-2.0	550-600 450-500	Spinel lherzolites, serpentinites, eclogitized metagabbro, metaroddingite, metabasalt, metasedimentary rocks	Serpentinite, chlorite-rich schist	High-strain serpentinite shear zones and low-strain zones with peridotite, high-pressure veins
Sivrihisar	93-80	1.5-2.6	450-550	Layers of metacarbonate, metachert and metabasalt (eclogite and blueschist). Serpentine lenses	Blueschist, quartzite, calc-schist.	Elliptical, folded lawsonite eclogite pods within blueschist, quartzite and calc-schist. Pods and lenses of metatuffs, metagabbro and serpentinite. Serpentine lenses surrounded by reaction zones of chlorite-lawsonite $\pm$ talc $\pm$ oxides $\pm$ carbonate.
Monviso	50-40	2.2-2.6	480-550	Mafic eclogites, Fe-Ti metagabbros, serpentinites, calc-schists	Serpentinite	Relatively preserved oceanic lithosphere cut by two major shear zones in which blocks are embedded in serpentinite, high-pressure veins in Fe-Ti metagabbros, eclogite breccias
Cima di Gagnone	Alpine	2.5-3	750-800	Chlorite harzburgite, garnet peridotite	Pelitic schists and gneiss	Ultramafic-mafic rocks occur in lenses 10-100s of m in size within pelite and gneiss