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An evaluation of reactive fluid flow and trace element mobility in subducting slabs

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Abstract

Permeabilities in the subducting slab appear to be too low and dihedral angles between fluid and relevant minerals too high to allow for porous flow, hence fluid channelization is critical for the understanding of subduction zone fluid fluxes. In this review we will outline how fluid channelization controls reaction rates and element redistributions during metamorphism of the subducting plate as well as trace element compositions of subduction-related fluids during flow.

Channelized fluid flow predicts that from a rock point of view, most formerly subducted material will show only very limited evidence for fluid flow, consistent with the rarity of observed high fluid fluxes in subduction-related rocks. Aqueous fluid produced by dehydration reactions will not percolate through large rock volumes, but rather will be carried away from the dehydration sites by a veining network. Indeed evidence for significant aqueous-fluid fluxes have been found in high-pressure veins with adjacent selvages. In such selvages, large lithophile elements (LILE's) generally show the highest mobilities, followed by light (L) rare earth elements (REE) and then heavy (H) REE. Compared to high field strength elements (HFSE), even Th shows higher mobilities.

From a fluid point of view, equilibrium between aqueous fluid and surrounding rock will only be approached at sites of fluid production and mineral reaction. However, this fluid can be significantly modified while moving upwards through a veining network where the wallrocks are out of equilibrium with the fluid. In a subducting slab, such reactive fluid flow can preferentially dissolve minerals and release their trace elements (e.g. Ba in phengite, Th and La in monazite). The degree of change in aqueous-fluid composition will depend on the amount of fluid–mineral surface interaction. The chemical exchange reactions will not be possible to model by trace element partition coefficients alone, instead future models need to incorporate kinetic parameters such as surface reaction rates.

Keywords: Reactive fluid flow; Trace elements; Subduction zones; Eclogites; Blueschists

1. Introduction

Subduction zones are the places on Earth where quantitatively the largest mass transfer rates exist and element fractionation occur between crust and mantle. The agents, which are central to these processes, are

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either aqueous fluids, supercritical fluids, or melts (Scambelluri and Philippot, 2001; Gao and Klemd, 2001; Schmidt and Poli, 2003; Plank, 2005; Kessel et al., 2005; for a definition of aqueous fluid, melt and supercritical fluids in relation to the second critical end point see Manning, 2004 and Hermann et al., 2006). Geochemical constraints from arc magmas indicate that a significant component of relatively fluid-immobile elements like Be and Th must come out of the slab (e.g., Morris et al., 1990; Plank, 2005); and experimental evidence shows that melts and supercritical fluids are efficient transport agents of such trace elements (e.g. Johnson and Plank, 1999; Kessel et al., 2005). However, field evidence found in partially dehydrated rocks shows that aqueous fluids can also serve as transport agents for most trace elements including Th (John et al., 2004, in press).

In the following review we want to describe a model for fluid flow within slabs that suggests that slab melting must not necessarily be invoked for mobilization of so-called fluid-immobile trace elements. As we will show, in order to scavenge elements from areas with relatively low overall fluid production (such as subducting slabs), it is critical that the fluid released by devolatilization reactions is highly channellized. A number of reviews have already discussed the role of high-pressure fluids (Manning, 2004) and its impact on eclogite-facies rocks in the field (Philippot and Rumble, 2000; Scambelluri and Philippot, 2001; Ague, 2003; Hermann et al., 2006). In this review we will focus on the evidence for reactive fluid flow in localized channel networks in high-pressure metamorphic terranes and its distinct chemical signature that is a direct counterpart to that in arc magmatism.

2. Fluid flow in subducting rocks

In subduction zones the hydrothermally altered, incoming oceanic plate (Fig. 1) descends into the mantle. During subduction, metamorphic reactions cause devolatilization reactions leading to eclogitization of the subducting crust and serpentine breakdown within the subducting lithospheric mantle. Most devolatilization reactions are strongly temperature dependent and occur as the temperature rises during ongoing subduction (Schmidt and Poli, 1998, 2003). In the upper part of the slab, the thermal gradient is inverted so that the sediments start to release water first, followed by the crust and then the mantle (Rüpke et al., 2002; Hacker et al., 2003). Aqueous fluids released from the lower layers of the subducting slab continually infiltrate upper layers, therefore, in a subducting oceanic plate, meta-

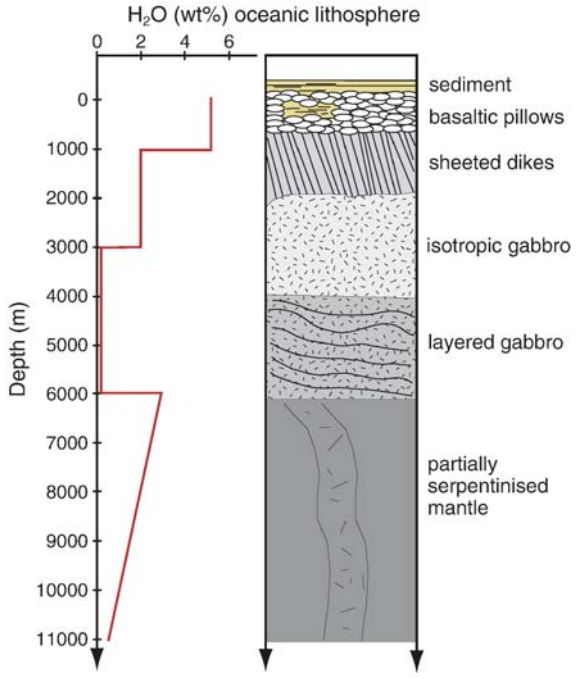

Fig. 1. Schematic cross section through the oceanic lithosphere at the onset of subduction (from Rüpke et al., 2004). Estimates on the H_2O content are based on estimates from Schmidt and Poli (1998).

mafic rocks will interact with fluids coming from the partly serpentinized mantle and metasediments will interact with fluids from both the dehydrating crust and mantle. Oceanic lithosphere layering, at slow and ultra-slow spreading centers, is however more complex due to extensive faulting. For example faulting often juxtaposes serpentinized mantle directly with the seafloor (e.g., Dick, 1989).

In any case, the question arises how does fluid flow occur? At the onset of dehydration only some minerals in subdomains of rocks will start to react, thus only minimal fluid is present and it will be unevenly distributed (Fig. 2A; see Miller et al., 2003 for a detailed model). Under the high pressures present at the relevant depths, permeabilities are very low and insufficient to allow percolative flow (Manning and Ingebritsen, 1999; Ague, 2003). The dihedral angle between water-dominated fluids and garnet and clinopyroxene is greater than 60° at elevated pressures and temperatures thus prohibiting an interconnected fluid network along grain boundaries (Watson and Brenan, 1987; Watson and Lupulescu, 1993; Mibe et al., 2003). Short-lived fluid pooling is most likely only possible during reactions in progress, as a decrease of solid volume, associated with dehydration reactions, increases porosity and hence permeability

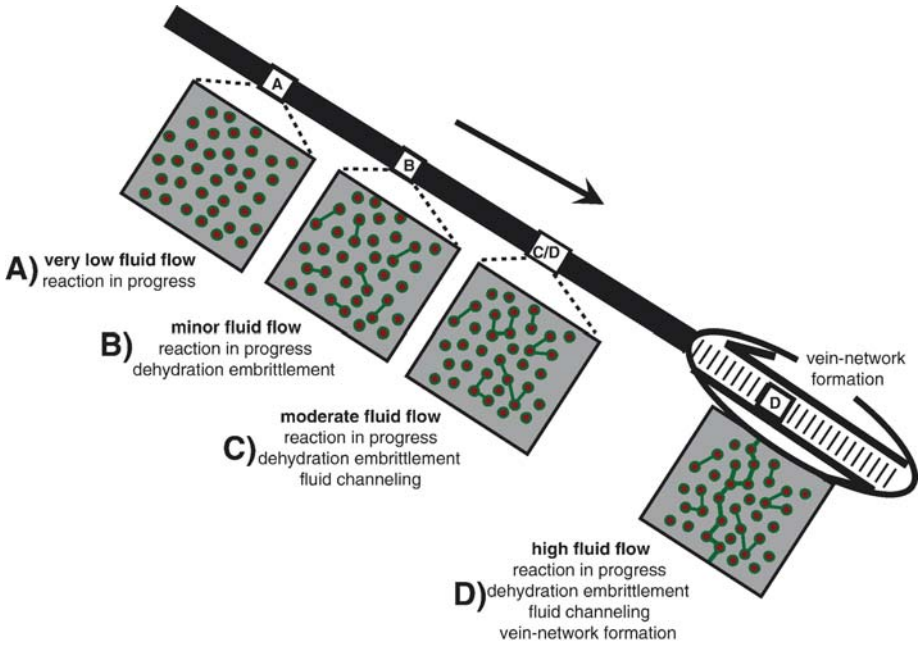

Fig. 2. Conceptual model for the development of fluid pathways during dehydration in low permeability rocks (modified after Miller et al., 2003).

(Rumble et al., 1982; Balashov and Yardley, 1998; Wang and Wong, 2003) (Fig. 2B). Ongoing fluid release results in high pore fluid pressure, which can cause dehydration embrittlement in the rock and probably triggers intermediate-depth earthquakes (Hacker et al., 2003; Jung et al., 2004; Jung and Green, 2004). Induced microfractures enhance and channelize the fluid flow within the domain where dehydration occurs (Miller et al., 2003) (Fig. 2C). If sufficient high volumes of fluid are reached, the elevated fluid pressure can open fractures allowing long-distance fluid transport (Yardley, 1986; Davies, 1999; Jung et al., 2004). Another possible pathway are shear zones which localize fluid flow (Breeding et al., 2004). These pathways allow fluids to escape the dehydrating system (Miller et al., 2003; Breeding et al., 2004; John et al., in press) (Fig. 2D). Fluid may pass through large volumes of rocks with little interaction via fast moving mobile hydrofractures (Bons, 2001). Veins formed by dehydration embrittlement have a short lifetime due to high lithostatic pressures (Camacho et al., 2005). However, fluid flow may occur episodically, thereby reopening these veins (Philippot and Selverstone, 1991; Davies, 1999; John and Schenk, 2003, 2006). Some of these veins have sharp contacts with their wallrocks (Fig. 2 of John and Schenk, 2006; John et al., in press), but some of theses conduits develop diffuse selvages, or fluid flow is channelized in shear zones where flow is more pervasive (Oliver and Bons, 2001; Breeding et al., 2004). Although selvages may not exceed a meter scale in thickness, they can line flow conduits for hundreds of meters (Ague, 2003; Klemd and Gao, pers. comm.). Selvages and shear zones can thus provide a place for interaction between long-distance fluids and their enclosing wallrocks, facilitating ion exchange and modifying the composition of fluids substantially along flow paths (Ague, 2003; Breeding et al., 2004; Molina et al., 2004; John et al., 2004, in press).

To gain a better understanding on the fluid flux quantities involved in subducting slabs, it is necessary to use a common terminology. Oliver (1996) defines a *closed system* as a rock–fluid system in which the rock does not record "significant" interaction with externally-derived fluids. Oliver sets an upper limit of a time-integrated reactive fluid flux of 10^3 mol cm^{-2} (or ca. 10^4 cm^3 cm^{-2}) as this is a value above which commonly investigated tracers like oxygen isotopes and H_2O–CO_2 equilibria in the rock are influenced by infiltrating aqueous fluid. As will be shown below, more sensitive tracers (e.g., concentrations and isotopic compositions of fluid-mobile trace elements) are influenced at lower fluid fluxes. We would like to stress that a time-integrated reactive fluid flux recorded by the rock record only predicts a minimum estimate on the total fluid fluxes involved. Some fluids will pass very fast through the system without reacting. It has been calculated that

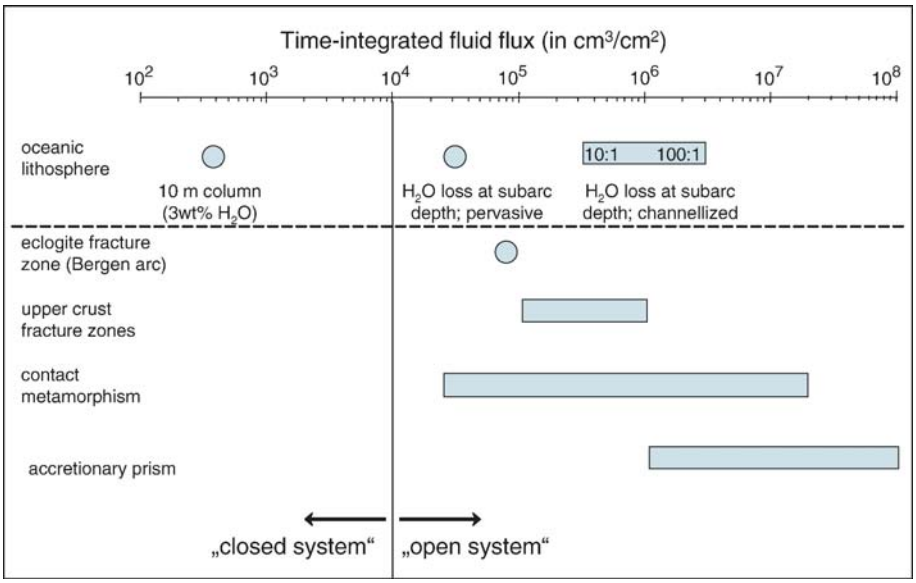

Fig. 3. Predicted and observed time-integrated fluid fluxes in different geological environments. Observed fluid fluxes (eclogite fracture zone, upper crustal fracture zones, contact metamorphism, accretionary prism) are from compilations of Gerdes and Ferry (1998), Philippot and Rumble (2000) and Ague (2003). Boundary between open and closed systems is from Oliver (1996). For predicted time-integrated fluid fluxes in the oceanic lithosphere see text.

fluids related to mobile hydrofractures can have buoyancy-driven ascent rates up to meters per second (Bons, 2001; Oliver and Bons, 2001).

Time-integrated fluid fluxes can be estimated for the fluid released at subarc depth with the following assumptions. Release of H_2O, the most abundant volatile, from the subducting oceanic plate has been calculated by Schmidt and Poli (1998). In a vertical column through the slab at the onset of subduction, they estimate $0.5–0.6\times10^5$ g H_2O m^{-2} in the basaltic layer, $0.11–0.18\times10^9$ g H_2O m^{-2} in the gabbroic layer, $0.01–0.02\times10^9$ g H_2O m^{-2} in the sedimentary layer and 0.21×10^9 g H_2O m^{-2} in the underlying mantle. Schmidt and Poli (1998) state that between 18 and 37% of the total H_2O budget will be lost at subarc depth (80–150 km) through dehydration reactions. From these values, a time-integrated fluid flux of ca. 3×10^4 cm^3/cm^{-2} at the slab–mantle interface results when it is assumed that all H_2O escapes upward at the top of this column (Fig. 3).

Such fluid fluxing can be classified as open-system behavior according to Oliver (1996), but it is on the lower end compared to classical areas of fluid flow systems (e.g. $10^5–10^6$ cm^3/cm^{-2} for upper crustal fracture zones, $2\times10^4–2\times10^7$ cm^3/cm^{-2} for contact metamorphic aureoles and $10^6–10^8$ cm^3/cm^{-2} for accretionary wedges, see Fig. 3 for references). The subducting slab is therefore *per se* not an area of high fluid fluxing. As outlined above, the important additional process is fluid channelization (Fig. 4). For example, if fluid flow is concentrated in veins, which make up 10% of an area, the time-integrated fluid flux in veins is higher by a factor of 10 than in a veinless area (at a vein density of 1% even by a factor of 100; for a conceptual model of vein spacing see DePaolo, 2006). At a vein density of 10% and 1%, time-integrated fluid fluxes in the veining systems near the top of the slab at subarc depth would be ca. 3×10^5 cm^3/cm^{-2} and 3×10^6 cm^3/cm^{-2}, respectively (Fig. 3). Such fluxes are comparable to areas of high fluid fluxing, and therefore can be clearly classified as an open system. From these simple calculations it is clear that significant chemical modification can be expected only in rock bodies affected by such high fluid fluxes.

However, channelization also implies that the majority of the rock body will experience small fluid fluxes (Fig. 4). Assuming that the basaltic layer of the oceanic crust has an average H_2O content of 3 wt% and that all fluid is lost by prograde metamorphism, a typical eclogite will not record a time-integrated fluid flux of more than 5×10^2 cm^3/cm^{-2} or 5×10^3 cm^3/cm^{-2} if the fluid is channelized in a vein network with a vein spacing of 10 m or 100 m, respectively (Fig. 3). It is obvious from such simple estimates that more than 90% of eclogite-facies rocks will record closed system behavior following the definition of Oliver (1996),

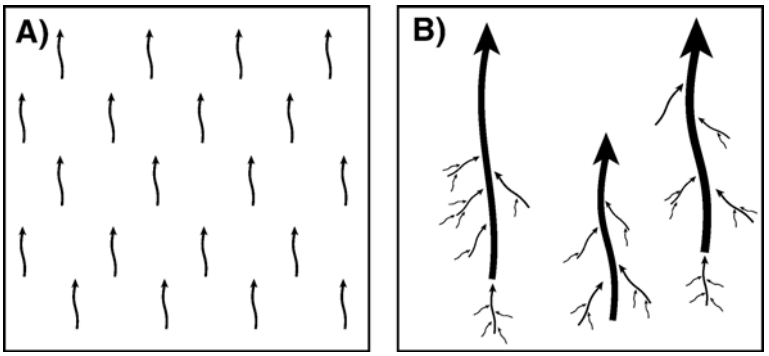

Fig. 4. Sketches illustrating the differences of pervasive (A) versus channelized fluid flow (B). The arrow size indicates the scale of fluid fluxes. Note that with the same total volumes of fluid and rock, channelized fluid flow causes larger volumes of fluid with smaller volumes of rock (higher time-integrated fluid fluxes) compared to the case of pervasive flow.

even though they derived from wet protoliths and have lost most of their structurally bound hydrogen. Such closed system behavior has been documented for several eclogite-facies localities around the world (e.g., Selverstone et al., 1992; Philippot and Rumble, 2000; Franz et al., 2001; Miller et al., 2001; Widmer and Thompson, 2001; Spandler et al., 2003; Busigny et al., 2003). We therefore dispute the notion that the common occurrence of "closed-system" behavior in many eclogite-facies rocks has been taken as a synonym for "fluid-immobility" in these rocks (e.g., Scambelluri and Philippot, 2001). Instead, in a system where overall fluid availability is low and fluid movement is channelized, most rocks *must* show "closed-system" behavior, while "open-system" behavior can only be traced in the rare cases where the fluid conduits are preserved.

Fluid recirculation (or convective circulation), advocated e.g. by Philippot (1993), Rubatto and Hermann (2003) and Spandler and Hermann (2006) for the observed cases of open-system behavior in high-pressure rocks, can only explain recorded fluid fluxes under special circumstances. Convective circulation requires a hydrostatic gradient in fluid pressure (Walther and Orville, 1982), which can only be maintained where permeable rocks are overlain by less permeable rocks (Etheridge et al., 1983). Even then, the rock strength constrains the size of convective cells to a few tens of meters (Yardley, 1986). However, rocks at high-pressure conditions are rarely permeable nor enclosed by less permeable and strong rocks (perhaps except in serpentine and mica-rich melange zones; Breeding et al. 2004). Additionally, fluid flow under prograde metamorphic conditions will be dominantly upward e.g., due to buoyancy contrasts (e.g., Hanson, 1997; Jung and Green, 2004), with the exception of fluid flow along induced permeabilities (cracks and shear zones) towards low fluid pressure boundaries, i.e. pathways of fluid escape (Miller et al., 2003). Thus fluid recirculation is not considered to be an important process under the conditions reviewed here (see also Ague, 2003).

3. Natural examples for fluid and trace element mobilities in high-pressure rocks

In the following section we will exemplify some principles outlined above and will combine field relations and petrographical observations with trace element data. The case studies are from different levels within the subduction zone where substantial fluid flow has been recorded (Fig. 5). These are at increasing depths: 1) within tectonic accretion zones (Cyclades, Greece), 2) during the dehydration of upper oceanic crust (Tianshan, China), 3) during serpentinite dehydration and fluid flow through the overlying lower oceanic crust (Zambezi Belt, Zambia). 4) Furthermore we will discuss a typical area where fluid fluxes were very low, but recordable. Here, near-equilibrium processes can be observed (Trescolmen, Switzerland). While the first example is from a mélange zone, the remaining examples are from coherent sequences.

3.1. Cyclades (Greece) — reactive fluid flow in accretion and mélange zones

In several studies of mélange zones and accretionary prisms evidence for extensive fluid flow was found to have occurred at the slab–mantle interface (Bebout and Barton, 1989, 1993; Manning, 1997). Intensive geochemical modification of mafic and ultramafic blocks in such zones due to fluid–rock interaction has been well-documented (Sorensen and Grossman, 1989, 1993; Bebout and Barton, 1989, 1993; King et al., 2003, 2006; Usui et al., 2006). This is interpreted to be related

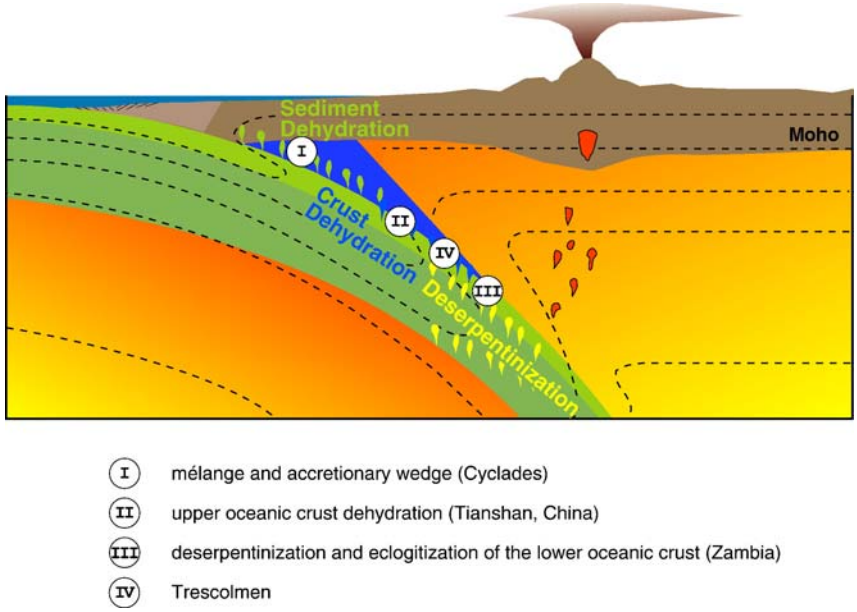

Fig. 5. Cross section through a subduction zone (from Rüpke et al., 2004) with locations of exposed high-pressure rocks discussed in the text. I.: melangé and accretionary wedge (Cyclades), II.: upper oceanic crust (Tianshan, China), III.: lower oceanic crust (Zambia), IV.: metapelite–metabasalt contact (Trescolmen).

to dissolution and precipitation of certain minerals by reaction with external fluids which are not in equilibrium with the infiltrated system (Breeding et al., 2003, 2004).

Within the ophiolitic mélange zone of the Cycladic blueschist belt several exposures show metasomatic effects in a setting in which large-scale faulting and folding during subduction juxtaposed metasediments, mafic and ultramafic rocks (Dixon and Ridley, 1987; Okrusch and Bröcker, 1990; Bröcker and Enders, 2001; Breeding et al., 2004; Keiter et al., 2004; Marschall et al., 2006). Blueschist- to eclogite-facies metamorphism occurred at temperatures between 500 and 550 °C and pressures of ca. 1.8 to 2.0 GPa (Trotet et al., 2001). Bröcker and Enders (2001) attributed the unusually high trace element concentrations (e.g., Zr=4950 ppm and Y=480 ppm) found in eclogites from Tinos to an infiltration of trace element rich fluids under eclogite-facies conditions. They found zircons formed along healed fractures; possible candidates for former infiltration pathways (Fig. 3e of Bröcker and Enders, 2001). Along with Tomaschek et al. (2003) and King et al. (2003), they speculate that HFSE were transported by an aqueous fluid through a fracture network to their new host.

On Syros, Breeding et al. (2004) and Marschall et al. (2006) investigated metasomatic alteration in mélange zones, occurring during exhumation at pressures of ca. 1.2 GPa and temperatures of 500–550 °C. Reaction rinds around metamafic blocks consist of omphacite, glaucophane, and/or chlorite. Breeding et al. (2004) document the interaction of fluids from meta-ultramafic mélange zones with metasediments along contacts. Unaffected metapelite contains phengite + sodic pyroxene + epidote + garnet + glaucophane + quartz + titanite + zircon + rutile. Close to the contact, glaucophane is more abundant, whereas chlorite, albite, magnetite, and apatite appear and phengite, epidote, sodic pyroxene, quartz, and garnet abundances decrease. Ratios among HFSE (Ti, Zr, Hf, Nb), Th, and rare earth element (REE) do not vary significantly across the layer, suggesting limited mobility for these elements. In contrast, LILE (K, Rb, Ba, Cs), Ca, Sr, U, and Pb are strongly depleted within the metasediments adjacent to the meta-ultramafic mélange, whereas Mg is enriched. This meta-ultramafic mélange contains low concentrations of LILE, U, and Pb, indicating that these elements were not exchanged locally, but instead were carried away by aqueous fluids flowing through the mélange. K, Rb, Ba, and Cs losses result from phengite dissolution during alteration. The dissolution of epidote, garnet, and clinopyroxene released Ca. Mg addition correlates with precipitation of new glaucophane and chlorite. Dissolution of epidote caused the mobilization of Pb and Sr. According to their findings Breeding et al. (2004) concluded that the dehydration of downgoing slabs

releases fluids that can flow through and react with metamorphosed ultramafic–mafic rock packages in mélange zones near slab–mantle interfaces. These fluids preferentially leach LILE, U, and Pb when they infiltrate and react with subducted metasedimentary rocks. Additionally, Marschall et al. (2006) found that fluid flow within the mélange zones on Syros can cause extreme $\delta^{11}B$ fractionation (up to +28.4‰), which is recorded in tourmalines formed at blackwalls between ultramafic mélange and metamafic blocks.

3.2. Tianshan (China) — reactive fluid flow in dehydration and transport veins; eclogitization of upper oceanic crust

The mafic high-pressure rocks of Tianshan (NW China) provide the opportunity to investigate "frozen" stages of ongoing dehydration and fluid flow occurring during blueschist- to eclogite-facies transition in subducting oceanic crust (Gao and Klemd, 2001; John et al., in press). They display an interconnected network of eclogite-facies veins derived by prograde blueschist dehydration, which provides insights into fluid–rock interaction and element mobility during dehydration and long-distance fluid flow. The Tianshan in NW China mainly consists of blueschist-, eclogite- and greenschist-facies metasediments and mafic metavolcanics (Gao et al., 1995, 1999; Gao and Klemd, 2003). According to their trace element composition, the mafic rocks resemble depleted to enriched mid-ocean ridge, ocean island and arc basalts (Gao and Klemd, 2003; John et al., in press). Blueschist and intercalated eclogites occur within greenschist-facies metasediments as small discrete bodies, lenses, bands, and up to several km thick layers. Locally the transition from blueschist to eclogite assemblages is gradual, indicating that both have experienced identical peak metamorphic conditions. Estimates on peak metamorphic conditions range between 480 and 580 °C at 1.8–2.1 GPa (Klemd et al., 2002; Wei et al., 2003).

A network of mm- to dm-wide and up to meter-long veins in massive prograde blueschist and eclogite indicates that a free fluid phase was present at eclogite-facies conditions (Gao and Klemd, 2001). The massive blueschist gradually transforms locally into eclogite-facies selvages (dehydration haloes) towards veins. The eclogitic wallrock that forms these selvages contains garnet and omphacite formed by prograde dehydration reactions, e.g., indicated by inclusions of hydrous blueschist-facies minerals in porphyroblastic garnet (Fig. 2 in Gao and Klemd, 2001). Dehydration haloes, gradually proceeding from omphacitite (up to several cm distance from the vein boundary) to eclogite, between vein and unmodified blueschist can be up to 50 cm wide. Gao and Klemd (2001) interpreted the aqueous, low-salinity fluid from which the vein minerals precipitated to have been derived from the blueschist host by means of dehydration reactions. O-isotope data support this interpretation because the fluid resulting from dehydration of blueschist has similar O-isotope signatures to the fluid that formed the veins and vein selvages (Gao and Klemd, 2001). Beside the above-described dehydration veins, the vein network of the Tianshan metabasites consists also of eclogite-facies veins which crosscut blueschist textures and display sharp interfaces with their blueschist host (Fig. 6a). The host rock of these veins shows no evidence of dehydration reactions, pointing to an external fluid source. These veins, and those shown in Fig. 6b and c are interpreted as high-pressure transport veins, most likely candidates for channelways of fluid escape (Miller et al., 2003; Ague, 2003; John et al., in press). Fig. 6a shows such an eclogite-facies transport vein, its blueschist host and a reaction zone (blueschist alteration zone, BAZ), which is located in the central part of the vein. The contact between vein and host is sharp and according to the vein characteristics described above, the vein minerals precipitated from externally-derived fluids. Thus, this sample allows for the investigation of the unaffected protolith, the vein formed from external fluids, and an alteration zone in which fluid and host reacted (BAZ). P–T estimates for the fluid infiltration predict values around 500 °C at 1.9 GPa (John et al., in press).

The blueschist mainly consists of glaucophane, micas, epidote, dolomite, titanite and garnet while the veins consist of omphacite, quartz and apatite. Within the BAZ, glaucophane, paragonite and dolomite have been replaced by omphacite and garnet. Epidote shows evidence for dissolution and re-equilibration/re-precipitation. Rock textures indicate that the infiltration of external fluids produced the transport veins, most likely through hydraulic fracturing. These fluids are interpreted to have also triggered the eclogitization of the blueschist alteration zone.

An almost twice as high Li concentration of the vein and the BAZ in comparison to the blueschist host indicates an external origin of the fluids enriched in Li. This is in accordance with relatively high concentrations of Li (as well as P and Pb) in the veins (see also John et al., in press). A strong depletion (from 40–80%) of all trace elements (except for Li, P, and Pb) can be observed in those parts of the host with which the passing fluid reacted (BAZ) (Fig. 7). Here, LILE and LREE were almost two times more effectively mobilized than HREE and HFSE. Dolomite resorption had the effect that ca. 75% of the total carbon was released as CO_2 into the

reactive fluid (John et al., in press). Klemd et al. (2005) and John et al. (in press) suggest that a migrating, channelized fluid with a low trace element load and high potential to form complexes most likely caused the observed mobilization (see also Manning, 2004). They argue that trace element mobilization occurred during mineral dissolution (glaucophane, titanite, paragonite, epidote and carbonates) and precipitation (mainly omphacite and minor garnet and a second generation of epidote) due to passing, trace-element-poor fluid at high fluid–rock ratios. In addition, the fluid composition (Si-, Al-, Ca-, Na- and F-rich; Gao and Klemd, 2001; John et al., in press) most likely hampered the formation of rutile in the alteration zones. This is probably due to complexation, which allowed significant trace element scavenging, including HFSE and Th.

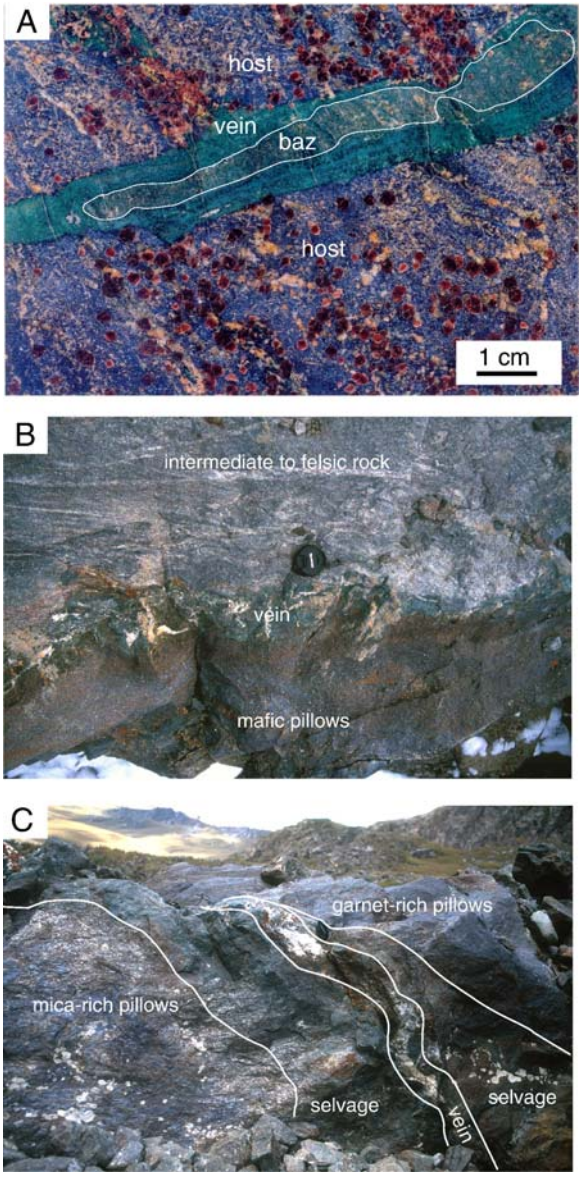

Fig. 6. Field pictures of the Tianshan mountains with eclogite-facies veins and garnet-bearing blueschist. A: The vein shows darker and paler bands indicating multiple opening and healing of the vein. The contact between vein and blueschist host is sharp with no selvage between blueschist and vein. This sample therefore contains a vein formed from externally-derived fluid. In addition a blueschist alteration zone (BAZ) is found within the central part of the vein in which fluid and host reacted to form the BAZ (see text for a more detailed explanation. Modified after John et al. (in press). B: Eclogite-facies vein formed along interface between blueschist-facies pillows (below) and intermediate to felsic rock showing eclogite-facies and blueschist-facies domains (above). An eclogite-facies selvage developed at contact to pillows. C: Eclogite-facies vein formed between blueschist-facies pillows of different compositions (one mica-, the other garnet-rich). Eclogite-facies reaction selvages (blueschist alteration zone, baz) developed along interfaces between vein and wall-rock lithologies.

3.3. *Zambezi Belt (Zambia) — reactive fluid flow during the gabbro-to-eclogite transformation; eclogitization of lower oceanic crust*

As indicated in Fig. 1, the lower oceanic crust is supposed to be almost dry. Its transformation to eclogite during subduction is often kinetically hampered because of sluggish solid–solid reactions rates (Wayte et al., 1989; Hacker, 1996; Austrheim, 1998; John and Schenk, 2003). Instead, infiltrating and passing fluids trigger, permit, and enhance the gabbro-to-eclogite transformation in lower oceanic crustal rocks (Hacker, 1996; Rubie, 1998; John and Schenk, 2003). In central Zambia fragments of such a former subducted lower oceanic crust are exposed and show evidence for fluid-induced eclogitization. Spatially associated gabbros, partially eclogitized gabbros, and eclogites are exposed along a ca. 200 km long palaeosuture zone. These mafic rocks form hills of ten to hundred meters in diameter. No evidence for prograde blueschist- or amphibolite-facies mineral assemblages was found in the eclogites. Instead gradual stages of the prograde gabbro-to-eclogite transformation are preserved by disequilibrium textures of incomplete reactions. Locally occurring fine-grain intergrowths of eclogite-facies minerals replacing plagioclase indicate the direct eclogitization of gabbroic precursors, whereas along fluid infiltration pathways complete eclogitization can be observed. Eclogitization occurred at 630–690 °C and 2.6–2.8 GPa and was accompanied by a channelized fluid flow that produced veins with peak metamorphic assemblages (John et al.,

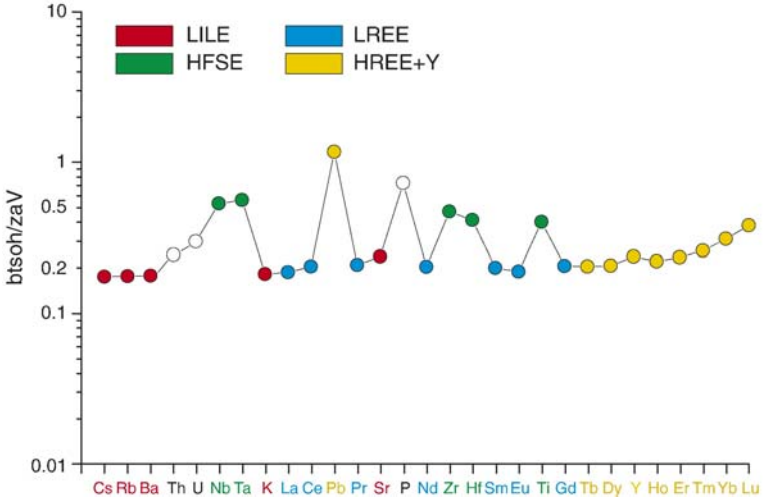

Fig. 7. Trace element results from blueschist alteration zone (baz) of Fig. 3a normalized to the composition of host close to the vein (host), showing that all trace elements were mobilized in the baz due to reactive fluid flow. Generally, trace elements occur in low concentrations in the blueschist alteration zone (ca. 0.2 times host), while the HFSE (ca. 0.5 times host) have little higher concentrations. Note that ca. 75% of the Th is mobilized from the baz. (LILE=red; LREE=blue; HREE+Y=yellow; HFSE=green). Figure modified from John et al. (in press).

2003; John and Schenk, 2003). The main process that transformed the gabbros to eclogites was fluid-controlled dissolution, transport, and precipitation (Engvik et al., 2001; Putnis, 2002; John and Schenk, 2003).

The reacting aqueous fluid had variable Cl concentrations, from low to high and locally up to brine compositions. The mafic rocks have both MORB-like trace element composition as well as initial Nd and Hf isotope compositions. In some eclogites however, LREE have been strongly fractionated from HFSE and HREE (Fig. 8), an effect that cannot be of magmatic origin but must have occurred during metamorphism. Garnet-whole rock ages based on the Sm–Nd (relatively mobile) and Lu–Hf (relatively immobile) isotope systems are identical, suggesting in conjunction with the petrological evidence described above that LREE were fractionated during eclogitization (John et al., 2004). Eclogitization was limited by fluid availability, and the flow of fluids through the rock is the most likely mechanism of LREE fractionation. Using mineral–fluid partition coefficients to calculate fluid–rock ratios reveal that if fluid–rock ratios are high the LREE will be fractionated, but if the ratios are low the LREE will not fractionate and remain indistinguishable from the magmatic signal. The fractionated rocks reacted with an amount of fluid up to 80% of their total mass to create the most depleted REE patterns. The lower gabbroic part of the oceanic crust is an unlikely source for such a large volume of fluid and thus it is likely that the fluid originated from the underlying serpentinized lithospheric mantle.

3.4. Trescolmen (Switzerland) — eclogite/metapelite contact; limited fluid flow

The concept of channelization of fluids necessitates that fluid fluxes are low in regions outside the major

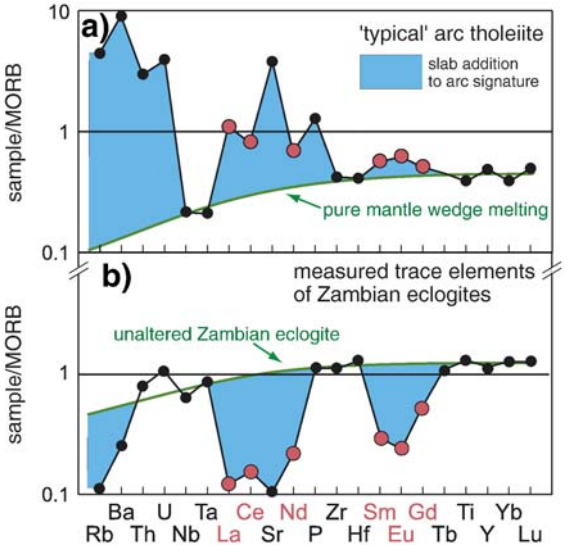

Fig. 8. Comparison of MORB-normalized patterns of 'typical' arc tholeiite (a) and Zambian eclogite (b) demonstrates that several of the same elements found in the slab component of arc magmas have been removed from those Zambian eclogites that experienced high fluid–rock ratios during eclogitization by reactive fluid flow. (LREE are highlighted). After John et al. (2004).

veining network. However in these regions, aqueous fluids generated by dehydration/decarbonation reactions must be transported out of the reactions sites to the veining network. In general, low fluid fluxes are difficult to document. Furthermore, evidence for fluids under eclogite-facies conditions are often obstructed by fluid infiltration and recrystallization during exhumation (e.g. Agard et al., 2002). Movement of small amounts of fluids at eclogite-facies conditions can be especially well studied on different scales in a one km^2 large area around the Lagh de Trescolmen (Switzerland), where numerous meter to decameter large eclogite bodies are found in a ca. 500 m thick garnet micaschist sequence. The eclogites show only minor evidence for amphibolite-facies overprinting, while the metapelites have been partly recrystallized at amphibolite-facies conditions, but eclogite-facies phases still dominate (high-Si phengite + kyanite + garnet + quartz, amphibolite-facies biotite–albite symplectites around phengite; Heinrich, 1982; Meyre et al., 1998). Low Na concentrations in the metapelites (Zack et al., 2003) may be responsible for the preservation of eclogite-facies textures in Trescolmen. Low Na concentrations reduce H_2O production from reactions like paragonite + quartz = albite + kyanite + H_2O. This reaction has been shown by Heinrich (1982) to be important for retrogression at amphibolite-facies conditions during exhumation. Instead, textures related with fluid movement at eclogite-facies conditions are omnipresent.

On a μm scale rehealed cracks in garnet cores with compositions of garnet rims coexisting with omphacite (Zack et al., 2002a) are manifestations of fluid flow through mineral microcracking (Erambert and Austrheim, 1993; Engvik et al., 2001). On a thin section scale growth of unstrained and chemically homogeneous neoblastic omphacites are facilitated by a dominance of fluid-mediated mass transfer over dislocation creep (Godard and Van Roermund, 1995; Zack et al., 2002a).

On a meter to decameter scale channelized fluid flow can be observed. High-pressure veins, characterized by a lack of amphibolite-facies rinds, can be found in almost each eclogite body. Most of them are quartz-dominated with a range of additional minerals forming sub-assemblages of their surrounding wallrocks. These minerals are in decreasing abundance: phengite, kyanite, omphacite, rutile and apatite. Interestingly, neither garnet nor amphibole has been found as vein minerals, although they are stable towards vein contacts (Heinrich, 1986). In one Mg-rich eclogite body, talc-rich veins (together with quartz, rutile and kyanite) have been found, where talc replacement by barroisitic amphibole points to minimal pressures of 2.2 GPa for the formation of these talc veins (Zack et al., 2001). So far, selvages around high-pressure veins (e.g. omphacite-rich areas) have not been observed (Becker et al., 1999). Veins found in Trescolmen are generally of local origin. This is indicated by minerals in veins always forming sub-assemblages of surrounding wallrock, with no trace of exotic minerals (e.g., phengite-free eclogites do not contain phengite-bearing veins (Zack et al., 2001). Furthermore, veins lack any selvages. Clear evidence for higher fluid fluxing in the Trescolmen area has not been found so far. However, the erratic occurrence of garnetites (90% garnet together with omphacite, quartz and high contents of rutile and zircon; Heinrich, 1983), which must be metasomatic in origin, may point towards areas of high fluid fluxing during eclogite-facies conditions (see John and Schenk, 2006). Furthermore, fresh garnet kyanite micaschists close to large eclogite bodies show microtextures of Th-mobility, which may also be explained by higher fluid fluxing. Here, corroded monazite grains are surrounded by apatite and allanite (Fig. 9), pointing to monazite breakdown by an external fluid (see Section 5). Th appears to be mobilized at least beyond the scale of a thin section as relictic monazite grains have 3.7 to 5.8 wt% ThO_2, while apatite and allanite have <0.6 and <0.1–3.6 wt% ThO_2, respectively (determined by EDS).

Barroisitic amphibole and paragonite formation in Trescolmen can be linked to fluid infiltration during high pressure, as they are only stable in eclogites during a certain part of the isothermal exhumation path for the

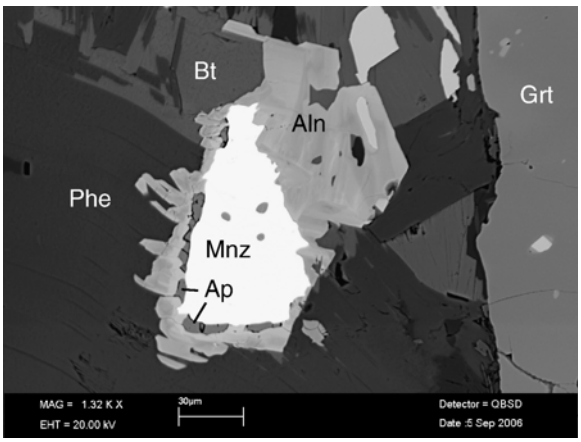

Fig. 9. Evidence for local mobilization of Th by aqueous fluids in fresh garnet micaschists from Trescolmen. Shown is a back scattered image of a corroded monazite grain surrounded by apatite and allanite, pointing to monazite breakdown by an external fluid. Th appears to be mobilized at least beyond the scale of a thin section as relictic monazite grains have 3.7 to 5.8 wt% ThO_2, while apatite and allanite have <0.6 and <0.1–3.6 wt% ThO_2, respectively (determined by EDS).

Trescolmen area (between ca. 2.0 and 1.4 GPa at temperature conditions of ca. 650 °C; Meyre et al., 1997, 1998; Zack et al., 2001), but were unstable at peak pressure conditions of ca. 2.4 GPa (Meyre et al., 1998). Barroisitic amphibole and paragonite are widely dispersed in Trescolmen eclogites and are partly aligned together with omphacite and partly texturally late (e.g. amphibole overgrowing oriented omphacite at a high angle, paragonite replacing kyanite; Zack et al., 2001). Frequently, barroisitic amphibole abundance in eclogites is higher at contacts adjacent to surrounding garnet micaschist, pointing towards a fluid source outside the eclogites. The clearest evidence for pervasive fluid flow derives from an eclogite contact with a decimeter-thick phengite vein (Fig. 10a). From the vein contact towards the interior of the eclogite, the modal abundance of amphibole steadily decreases for at least 40 cm from ca. 6 modal% to 2 modal%. The mm-sized amphibole crystals are regularly spaced and occur neither clustered nor aligned. Interestingly, potassium was also mobilized, as phengite is found only within the outermost 10 cm of this eclogite body (Fig. 10b).

The major element composition of the eclogites closely follows differentiation trends found in mid-ocean ridge basalts, with the exception of elevated Na and K contents, which are interpreted to originate from high and low temperature hydrothermal alteration, respectively (Zack et al., 2002a, 2003). These findings are consistent with the petrographical observations that fluid flow was limited to high-pressure conditions. However, fluid fluxes were high enough to allow Cs–Rb–Ba exchange on a meter-scale between amphibole in eclogite and phengite in enclosing garnet micaschist (Zack et al., 2001). Additionally, equilibrium was reached on a thin section scale for a range of trace elements (Sr, Pb, REE) between omphacite, barroisitic amphibole, phengite and apatite (Zack et al., 2002a). This observation indicates that fluids facilitating this equilibrium must also be in trace element equilibrium with coexisting mineral phases.

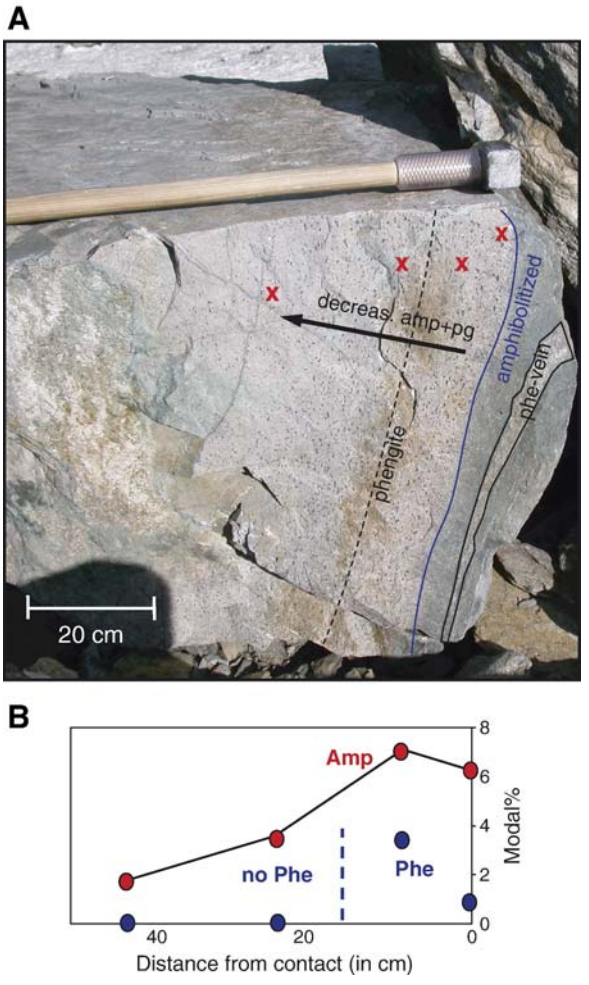

Fig. 10. Evidence for fluid infiltration in eclogites from Trescolmen. A) contact between phengite vein and eclogite. Red crosses are sample sites. Black dots in eclogite are barroisitic amphiboles. B) Results from thin section mapping of samples indicated in A). Modal abundances of phengite and amphibole are calculated from ca. 300000 WDS analyses for each sample (for analytical details see Zack et al., 2002a,b). Disappearance of phengite is marked by dotted lines in A) and B).

4. Trace element behavior during reactive fluid flow under low-T/high-P conditions

Blueschist- and eclogite-facies rocks away from areas of high fluid fluxes only show significant depletions in B, N and LILE concentrations (Moran et al., 1992; Becker et al., 2000; Mingram and Bräuer, 2001) as well as lower δ^7Li (Zack et al., 2003), lower δ^{11}B (Peacock and Hervig, 1999) and higher δ^{15}N (Mingram and Bräuer, 2001) compared to their various protoliths. Significant depletion can be defined as the depletion of a residuum beyond the scatter associated with the rock protolith composition. With this definition, several trace elements (REE, HFSE) generally do not show significant depletions when comparing high-pressure rocks and potential protoliths (Tribuzio et al., 1996; Spandler et al., 2003). However, apparently unchanged compositions only give limited information about the trace element composition of the fluids involved. Simple Rayleigh-distillation calculations $\left(C_s = C_0(1-F)^{\frac{1}{D}-1}\right)$ demonstrate that even a fluid loss of 3 wt% (F=0.03) in which a fluid is enriched 10× (D=0.1) in a certain trace element compared to the rock

will leave the residual rock with a concentration of more than 75% of this trace element (C_s / C_0). This is typically not beyond the scatter associated with the protolith composition (see also discussion/reply by Liebscher, 2004 and Spandler et al., 2004).

Mass balance studies of selvages and unaltered host rock allow the calculation of enrichment/depletion factors of the trace elements of interest during fluid flow. In the case of the Tianshan veining system, up to 80% of LILE's were mobilized (John et al., in press). The most valuable results from such studies are estimates about trace element fractionation. At conditions of ca. 500 °C and 1.2 GPa (Syros), LILE, Sr, Pb and U were significantly more depleted than HFSE, while REE and Th were not fractionated from HFSE (Breeding et al., 2004). At conditions of ca. 500 °C and 1.9 GPa (Tianshan), LILE were also fractionated from HFSE (John et al., in press). However, here Th and REE were significantly more depleted than HFSE, indicating e.g., that Th was clearly carried away by a H_2O-rich fluid (at least 200 °C below the solidus of SiO_2-rich melts). It is important to stress that direct observation of preferential mobilization of LILE over REE as well as preferential mobilization of LREE over HREE (John et al., 2004, in press) caused by aqueous fluid strongly support models that interpret elevated LILE/REE and LREE/HREE in volcanic rocks as a fingerprint for a subduction component caused by aqueous fluids (e.g. Gill, 1981; McCulloch and Gamble, 1991).

Hence, it can safely be assumed that trace elements can be mobilized and fractionated during reactive fluid flow in subduction zones, but what are the mechanisms that control the trace element behavior? It is evident that whenever external fluids dominate the chemical system, mineral assemblages of the affected rock body will respond to the chemical changes. Under the relatively low temperature conditions prevailing during slab dehydration, diffusional exchange of elements between mineral and fluid will be minimal, even though reactions are enhanced by dynamic recrystallization of minerals as observed in Trescolmen (Zack et al., 2002a). Instead, dissolution and/or precipitation of certain mineral phases will occur when fluids encounter changing temperature, pressure and/or compositional conditions (Austrheim, 1998; Putnis, 2002; John and Schenk, 2003). Hence, mobilization of a certain trace element depends on whether its dominant carrier phase will be dissolved and/or precipitated and on the kinetics of this process. Even in high-temperature systems, bulk reactions and the access to grain interiors (and access to inclusions in these grains) are limited by grain boundary migration (Baxter and DePaolo, 2002a,b). Thus it might be that only the outermost parts of minerals are dissolved, whereas the inner parts remain pristine. This would have a strong effect on elements which are often strongly incorporated in cores of zoned minerals, such as HREE in garnet and LREE in epidote-minerals (e.g., John et al., in press). Furthermore, the potential of a fluid for scavenging elements from a reaction domain correlates with its potential for complexation and clustering and is thus a function of the amount of ligands such as OH^-, H^+; Cl^-, F^- and polymers present (Manning, 2004). Flow velocities may be another controlling factor in combination with the kinetics, because if nucleation kinetics are slow and nucleation sites not already present, elements in solution may be transported away from the reaction site of mobilization at high flow velocities.

Several studies that attempt to estimate fluid fluxes by studying major and trace element compositions of veins, selvages and/or otherwise fluid-influenced high-pressure rocks rely on experimentally determined solubilities and/or partition coefficients (e.g., Rubatto and Hermann, 2003; John et al., 2004). Experimental conditions of mineral/fluid partition coefficients cannot be easily transferred to natural conditions. Temperatures of experiments designed for mineral/fluid trace element partitioning studies are often ≥ 900 °C (e.g., Brenan et al., 1995; Stalder et al., 1998). Exceptions are studies of Green and Adam (2003) and Kessel et al. (2005), where experiments as low as 700 °C were performed, and here, the fluid composition in equilibrium with the experimental run products is only directly measured by Kessel et al. (2005). However, most fluid loss through dehydration occurs at 400–600 °C. Furthermore, the importance of parameters like increasing polymerization of alkali aluminosilicates with increasing pressure (see Manning, 2004) and complexation through Cl and F anions (Keppler, 1996) have not been investigated systematically for their influence on trace element partitioning at the important P–T conditions (2–4 GPa; 400–600 °C).

The use of partition coefficients in a dynamic system requires that the kinetics are fast enough to reach equilibrium. Kinetic parameters are not available for the pressure–temperature conditions of interest, however, in a Barrovian sequence, reaction rates between an intergranular fluid and plagioclase at ca. 600 °C and 0.9 GPa have been calculated to be on the order of 10^{-7} gram of solid reacted per gram of solid per year (Baxter and DePaolo, 2000). At such conditions approach to local equilibrium requires several million years, and thus Baxter and DePaolo (2002a,b) concluded that equilibrium may not be closely approached in dynamic metamorphic systems if significant changes in

P–T–X occur over shorter timescales. Even reaction rates several orders of magnitude higher would not be sufficient to reach equilibrium between a vein and a passing fluid at eclogite-facies conditions at the probable time scales of tens of years (Camacho et al., 2005). Consequently, near-equilibrium conditions may only exist at the sites where mineral reactions take place i.e. at the grain boundaries or other, highly reactive micro-domains (Engvik et al., 2001; John and Schenk, 2003). In summary, mobilities of trace elements are mainly controlled by the stability of their carriers under the given conditions and the solubility of these trace elements in the fluid. In reactive fluid flow, two trace elements can be strongly fractionated from each other if 1) more than one mineral is the major carrier of these elements, 2) the two trace elements occur in these minerals in different ratios, and 3) some of these minerals are stronger affected by the fluid than the other carriers.

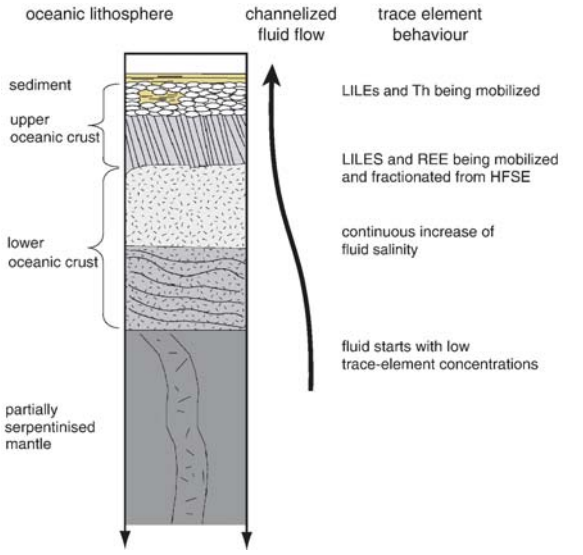

Fig. 11. Conceptual drawing of compositional change of fluids passing through the oceanic lithosphere. For further explanation see text.

5. Implications for origin of island arc signatures

As pointed out in the previous sections, in areas of channelized fluid flow, non-equilibrium processes may be much more common than assumed in most subduction zone models. There is good evidence for near-equilibrium conditions only at the sites where fluids are released by dehydration reactions (Zack et al., 2002a). Trace element fluid composition from these sites may be estimated by applying appropriate equilibrium partition coefficients between minerals and fluid. Instead, equilibrium processes are rare in open systems such as dehydrating slabs, where fluids from different sources have to pass through chemically different lithologies. Furthermore, fluid flow along a gradient of increasing temperature, as is probably common in subducting slabs, generally increases element solubility (e.g. Manning, 1994, 2004). Thus, significant modification of such fluids will occur while rising within a veining network through the subducting slab into the overlying mantle by reactive flow (e.g., Gorman et al., 2006).

Reaction progress depends on the amount of material with which the fluid interacts and on the time scales of interaction. This is partly dependent on the geometry (fractal behavior) and longevity (transient versus long-lived) of the vein network (Manning, 1994; Oliver and Bons, 2001) and the thickness of lithologies through which the fluid travels. Fig. 11 illustrates schematically the possible chemical uptake and element fractionation occurring by fluids released during serpentinite breakdown at the bottom of a subducting oceanic plate column. The fluid will interact with the passing rocks according to the described field evidence. Serpentine breakdown releases a fluid with overall low trace element concentration (except Li and B: Morris and Ryan, 2003; Scambelluri et al., 2004b; but see Hattori and Guillot, 2003 and Scambelluri et al., 2004a for serpentinites as potential storage sites for As, Sb, LREE and LILE). This fluid may cause eclogitization of the lower oceanic crust during its passage (John and Schenk, 2003) and thereby mobilizing LREE, i.e. fractionating LREE from HFSE and HREE (John et al., 2004). It should be noted that the passage of fluid through the fluid-undersaturated lower crust will lead to formation of hydrous phases (Schmidt and Poli, 2003). During hydration, H_2O will be preferentially lost in relation to Cl (e.g., Markl et al., 1998), so that an already relatively saline fluid (Scambelluri et al., 1997) will be even more saline after leaving the lower oceanic crust. Further flow passing through already eclogitized upper oceanic crust will most likely cause an enrichment of Ca, Na, Al and Si (Manning, 2004; Gao and Klemd, 2001) along with mobilization of LILE and REE (Breeding et al., 2004; John et al., in press). Passage of fluid inside the mantle wedge will lead to further modification of its chemical composition (see King et al., 2003, 2006; Scambelluri et al., 2006), but this is beyond the scope of this contribution.

Beside this more general model, applying reactive fluid flow to the chemical changes in subduction zones as proposed in this contribution has further predictive potentials. It can, for example, offer an explanation for the positive world-wide correlation between the amount of Ba in subducted sediments and Ba concentration in

corresponding island arc basalts (Plank and Langmuir, 1993). Traditional application of equilibrium partition coefficients would predict that the higher the Ba signal in island arc volcanoes is the higher is either the fluid component or the *concentration* of Ba in the source. However, this is not what is observed in nature. It is rather the total *amount* of subducted Ba which correlates with the Ba signal in island arcs (Plank and Langmuir, 1993). Fluids released by dehydration processes from metabasalts and serpentinites deep within the subducting slab will have very low concentrations of potassium. When such phengite-undersaturated fluids are passing through the overlying column, they will dissolve more phengite the more extensively they interact with phengite-rich material, i.e. dependent on the sedimentary column thickness. Since phengite is the principal carrier for Ba (as well as for Cs and Rb; Zack et al., 2001) in subducting slabs, the fluid will contain more Ba the more phengite is dissolved. The principal assumption here is that the channelized fluid passing through the sedimentary pile will never fully equilibrate with phengite and hence will not be completely buffered by phengite.

A similar scenario can be envisaged for Th and Th/La ratios. Monazite (LREE-phosphate with several wt% Th) is the most significant carrier for Th in subducting slabs. Monazite is common in Ca-poor metasediments of almost all metamorphic grade (Spear and Pyle, 2002), even under UHP-conditions (e.g. Terry et al., 2000). In contrast, it is nearly absent in both ultramafic and mafic assemblages (Spear and Pyle, 2002). It is likely that fluids in the subducting slab originating from the mafic part of the slab will dissolve monazite from overlying metasediments by reactive fluid flow. Relatively Ca-rich fluids derived by dehydration from the mafic systems (e.g. Gao and Klemd, 2001) will change the mineral composition to one in which apatite (Ca-phosphate) and allanite (Ca-LREE-silicate) form at the expense of monazite (Finger et al., 1998; Grapes et al., 2005). Apatite has usually 3 to 5 orders of magnitude lower Th and La concentrations than monazite at lower Th/La ratios (0.01–0.03 in apatite versus 0.3–0.7 in monazite), while allanite contains wt.% La and thousands of ppm Th at Th/La ratios similar to those of monazite (Finger et al., 1998; Spear and Pyle, 2002; Zack et al., 2002a; Hermann, 2002). Mass balance therefore requires that monazite replacement by allanite and apatite will release Th, and furthermore leading to high Th/La ratio in the fluid. Reaction textures in Barrovian-type metamorphic rocks indicate that the released Th can not be taken up by the fluid, since minute thorite grains form directly in the former monazite site. However, similar reaction textures in high pressure metapelites from Trescolmen are lacking thorite (Fig. 9), indicating that Th has been carried away by an aqueous fluid. This confirms studies by John et al. (in press) who showed that there is indeed evidence for Th mobilization by fluids in reaction zones of dehydrating mafic blueschists, which may correspond to dissolution of Th-rich allanitic cores, still present in epidote-minerals of the unaffected wallrock. Therefore, combining natural observation with theoretical consideration, it is likely that fluids from the mafic slab interacting with large volumes of monazite-bearing metasediments can release significant amounts of Th and La with high Th/La ratios, a characteristic feature so far only attributed to sediment melts (Johnson and Plank, 1999; Plank, 2005).

One key question remaining is to what degree Th and other "immobile" trace element concentrations in high-pressure fluids are controlled by dissolution rates and/or by the solution capacity of the fluid. In terms of dissolution rates, there is no experimental data on accessory mineral (e.g., monazite) response to various HP aqueous fluids. We can only qualitatively state that in HP metapelites, infiltrating fluids are capable of dissolving monazite. Estimates on maximum solubility of Th in aqueous fluids are difficult to calculate. Aqueous fluids in equilibrium with a metabasaltic assemblage contain 2.5 ppm Th at experimental conditions of 700 °C and 4.0 GPa (Kessel et al., 2005). Such a concentration is sufficient to explain Th levels in average island arc magmas (0.8 ppm; McCulloch and Gamble, 1991) by adding aqueous fluids with 1.9 to 3.2 ppm Th to the mantle wedge source; employing simple batch melting with a degree of melting of 10% and assuming 3% to 5% aqueous fluid addition (from Wallace, 2005) to a depleted mantle with 0.01 ppm Th (from Salters and Stracke, 2004).

As a final remark we want to emphasize that there is considerable evidence from natural examples that trace elements are indeed mobile in aqueous fluids. We do not question the capacity of supercritical fluids and melts as trace element carriers. However, the arising picture is that trace elements (including Th and REEs) are mobile in aqueous fluids below 650 °C. Therefore, a hot slab – shown in several recent studies referring to geochemical data to develop thermal models of subduction zones (e.g., Kelemen et al., 2003; Arcay et al., 2005; Conder, 2005) – may not unequivocally be required to explain the slab signature in island arc volcanoes.

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