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# Deep fluids in subduction zones

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## Abstract

The fluid inclusions preserved in high and ultrahigh pressure rocks provide direct information on the compositions of fluid phases evolved during subduction zone metamorphism, and on fluid–rock interactions occurring in such deep environments. Recent experiments and petrologic studies of eclogite–facies rocks demonstrate that stability of a number of hydrous phases in all rock systems allows fluid transport into the mantle sources of arc magmas, as well as into much deeper levels of the Earth’s mantle. In eclogite–facies rocks, the presence of large ion lithophile elements (LILE) and light rare earths (LREE)-bearing hydrous phases such as epidote and lawsonite, together with HFSE repositories as rutile and other Ti-rich minerals, controls the trace element budget of evolved fluids and fluid-mediated cycling of slab components into the overlying mantle.

Studies of fluid inclusions in eclogite–facies terrains suggest that subduction mainly evolves aqueous solutions, melts being produced only locally. Eclogite-facies rocks diffusely record processes of fluid–melt–rock interactions that exerted considerable control on the element and volatile budget of subduction fluids. Trace element fractionation during such interactions needs to be tested and quantified in more detail to achieve the ultimate compositions actually attained by fluids leaving off the slab. Variably saline inclusions with minor CO<sub>2</sub> and N<sub>2</sub> are trapped in rock-forming high pressure minerals; brines with up to 50% by weight dissolved solute are diffusely found in veins. The latter inclusions are residues after fluid–rock interactions and deposition of complex vein mineralogies: this evidence suggests increased mineral solubility into the fluid and formation, at a certain stage, of silicate-rich aqueous solutions whose geochemical behaviour and transport capacity can approach that of a melt phase. This is supported by experimental work showing high solubility of silicate components in fluids at high pressures. However, natural examples of inclusions trapping such a fluid and quantitative analyses of its major and trace element composition are not yet available.

Fluids in high and very high pressure rocks do not move over large scales and the channelways of fluid escape from the slab are not yet identified. This suggests that only part of the slab fluid is lost and returned to the surface via magmatism; the remaining trapped fraction being subducted into deeper levels of the upper mantle, to renew its budget of substances initially stored in the exosphere.

*Keywords:* Fluid inclusions; Subduction zones; Eclogite–facies metamorphism; Fluid–rock interactions; Chlorine; Oxygen isotope

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## 1. Introduction

Subduction of surficial terrestrial materials is accompanied by metamorphic changes resulting in continuous fluid production. These processes play a primary role in the genesis of magmas at convergent plate margins and attract the interest of many earth scientists. However, due to uncertainties in reproducing the conditions of subduction during experiments, there are different viewpoints on the nature of subduction fluids and their pathways in the slab and overlying mantle. The whole debate is hampered by the paucity of natural materials available for analysis and by the limited memory that high- and very high-pressure rocks preserve of their subduction histories, due to diffuse retrograde overprint acquired during exhumation.

Studies of oceanic rocks and of eclogitized ophiolites indicate that, prior to subduction, the slab-forming materials can be considerably altered by surficial fluids, trapped in pore spaces and in fluid inclusions, or bonded as components in mineral lattices. Rock compaction and devolatilization reactions at the initial stages of burial produce low-salinity, CO<sub>2</sub>- and CH<sub>4</sub>-bearing aqueous fluids (Kastner et al., 1991). At deeper levels, devolatilization and dehydration-melting reactions control the depth and abundance of fluid pulses, and several models have

been proposed to explain the pathways of deep fluids (Fig. 1). Some authors (Peacock, 1990; Bebout and Barton, 1993) propose that dewatering between 60 and 120 km causes massive discharge of water into the mantle overlying the subducting slab. In contrast, Philippot (1993) contended that most of the water is released at shallower levels (0–50 km) and that only a small fraction of the initial water (10%) is transferred into the subarc mantle via siliceous fluids and/or hydrous melts. Finally, a residual fraction of the slab fluid can be further subducted to deeper mantle levels (Fig. 1). In any case, the arc volcanoes above subduction zones represent compelling evidence that fluids infiltrate the mantle causing its hydration, metasomatism and partial melting.

The metasomatic effects of fluids in these mantle regions are recorded by the compositions of island arc basalts, reflecting their mantle sources. Compared with MORBs (Mid Ocean Ridge Basalts), arc basalts display depletion in high field strength elements (HFSE: Ti, Zr, Nb; Fig. 2A) relative to large ion lithophile elements (LILE: Sr, K, Ba) and light rare earths (LREE). Such an imprint is explained by melting of MORB-type mantle enriched in LILE relative to HFSE after equilibration with metasomatic agents escaping the slab (Gill, 1980; Kelemen et al., 1993; Hawkesworth et al., 1993; Brenan et al., 1994). The nature of these mobile

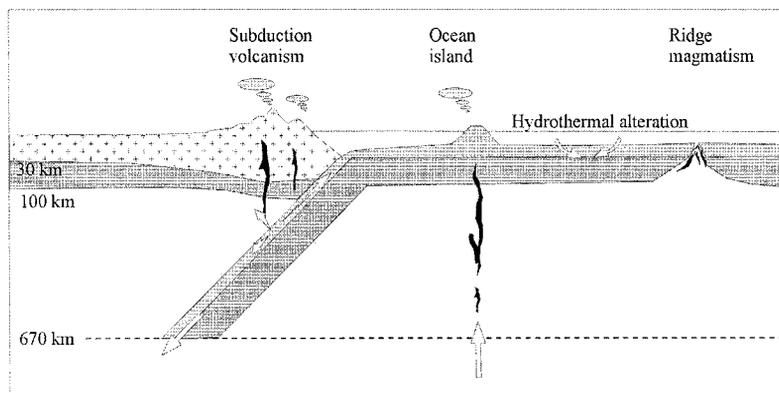


Fig. 1. Diagrammatic model showing burial of oceanic lithosphere along a subduction zone. Surficial hydrothermal alteration of the oceanic crust allows uptake of volatiles successively released during the burial process. The altered oceanic crust loses part of its water during eclogitization and several possible pathways are envisaged by the small arrows in the cartoon. The water released may: (i) cross the slab–mantle interface and hydrate the overlying mantle wedge; (ii) migrate up the subduction zone; (iii) continue its burial path into deeper levels of the mantle and feed it of (exsogenic) water and associated elements. The dehydration process is somehow accompanied by interaction of released fluids with mantle rocks, causing mantle metasomatism, partial melting and associated subduction volcanism. Part of the residual water injected into the deeper mantle may afterwards be recycled during OIB- and MORB-type magmatism.

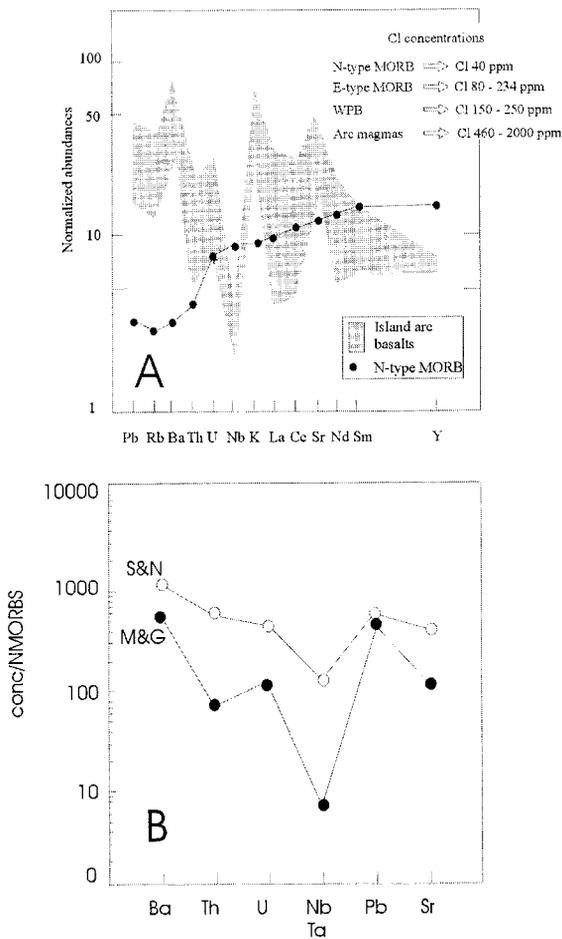


Fig. 2. (A) incompatible element abundances in island arc basalts compared with those in MOR-type basalts, normalized to primordial mantle values (after Wilson, 1989). (B) trace element compositions of slab-derived metasomatic agents. The diagram compares the slab component from McCulloch and Gamble (1991) and the trace element enriched hydrous component in the Marianas back-arc from Stolper and Newman (1994).

phases is yet uncertain, since they may either consist of hydrous silicate melts (Green and Ringwood, 1968), or of aqueous fluids (Tatsumi et al., 1986). A third alternative is that increasing solubility of silicates in aqueous solutions at high pressures and temperatures may generate highly concentrated siliceous and alkaline solutions: it has been recently proposed that such solute-rich fluids may behave as melt-like agents for mantle metasomatism (Massonne, 1992; Philippot, 1996). Quantitative estimates (Stolper and Newman, 1994; McCulloch and Gam-

ble, 1991) show that metasomatic agents are enriched in Ba, Pb and may display different fractionation of Th, U, Nb, Ta, Sr (Fig. 2B) relative to melts: the latter variations are thought to reflect the different nature of mobile phases, with silicate melts being richer in Nb, Ta, Th, U than hydrous fluids (see discussions in Langmuir, 1994; Brenan et al., 1995). Such fluid compositions are the result of complex flow and interaction histories into the mantle, and may be different from fluids coming off the slab. At present, it is yet uncertain whether the slab or the mantle wedge dominates in controlling the compositions of fluids that ultimately fertilize the sources of arc magmas (Hawkesworth et al., 1993; Brenan et al., 1995; Kelemen et al., 1990).

This paper aims at reviewing the above features, particularly in light of fluid inclusion studies in high- and very high-pressure rocks; the purpose is to clarify some aspects concerning the nature of these fluids and the processes occurring during percolation in the slab. Emphasis is given to the following key points: (i) the depths of fluid release; (ii) the nature and compositions of fluids, (iii), the fluid pathways and scale of motion; (iv) the origin and role of some important components like chlorine.

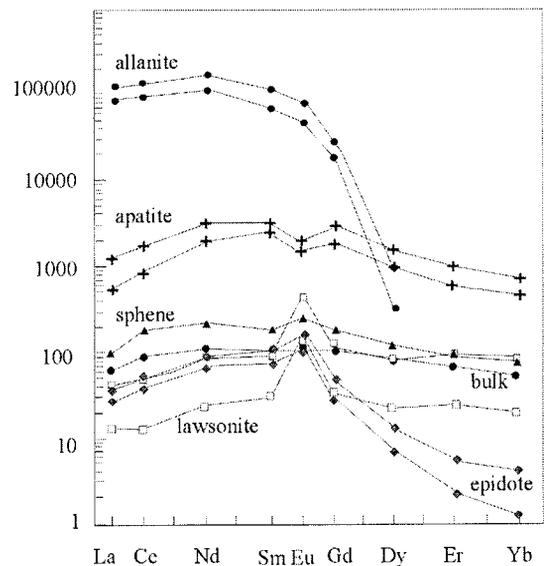


Fig. 3. Rare earth element compositions of hydrous phases in eclogites. Data on allanite, apatite, lawsonite and epidote (also reported is the bulk composition of host eclogites) after Tribuzio et al., (1996); sphene composition is after Sassi et al. (1996).

## 2. Depths of fluid release

Geophysical data indicate that the slab reaches 100–150 km depth below arc volcanoes (Gill, 1980). In the late 1980s and early 1990s, studies of the dehydration of subducting slabs emphasized a major fluid pulse at rather constant depth of 70–80 km, grossly coincident with the breakdown of amphibole (Tatsumi, 1989; Davies and Bickle, 1991). As a consequence, the slab was considered as essentially dry in the source regions of calcalkaline magmas, water being lost at shallower levels to hydrate the overlying mantle wedge. Downward transport of this altered mantle by corner flow ultimately led to melting as the solidus of amphibole–chlorite peridotite was reached (Tatsumi, 1989).

More recent experiments reveal that other hydrous phases (lawsonite, zoisite–clinozoisite, chloritoid, staurolite, phengite and antigorite) can transport water much deeper than amphibole (Schreyer, 1988; Pawley and Holloway, 1993; Poli and Schmidt, 1995;

Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1992; Schmidt, 1996; Schmidt and Poli, 1998). Part of the water evolved during amphibole breakdown is reincorporated into new hydrous phases (chloritoid, zoisite–clinozoisite, lawsonite), thus allowing storage of 1 wt.% bulk water to 200 km (Poli and Schmidt, 1995). Moreover, phengite stability to about 300 km in these systems, allows deeper transfer of water and potassium (Schmidt, 1996). These hydrous minerals are also carriers of trace elements relevant for metasomatism of subarc mantle (Fig. 3). Epidote-group minerals can be enriched in LREE (zoisite–clinozoisite up to 100 times per chondrite; allanite to  $10^5$  times per chondrite), as can lawsonite and apatite (10 to 100 times per chondrite); lawsonite can also contain 2500 ppm Sr (Tribuzio and Messiga, 1994; Tribuzio et al., 1996). Aluminous titanite in coesite eclogites from Dabieshan (Central China) is enriched in LILE, LREE, MREE (100 times per chondrite) and HFSE with respect to coexisting clinopyroxene and garnet (Sassi et al., 1996).

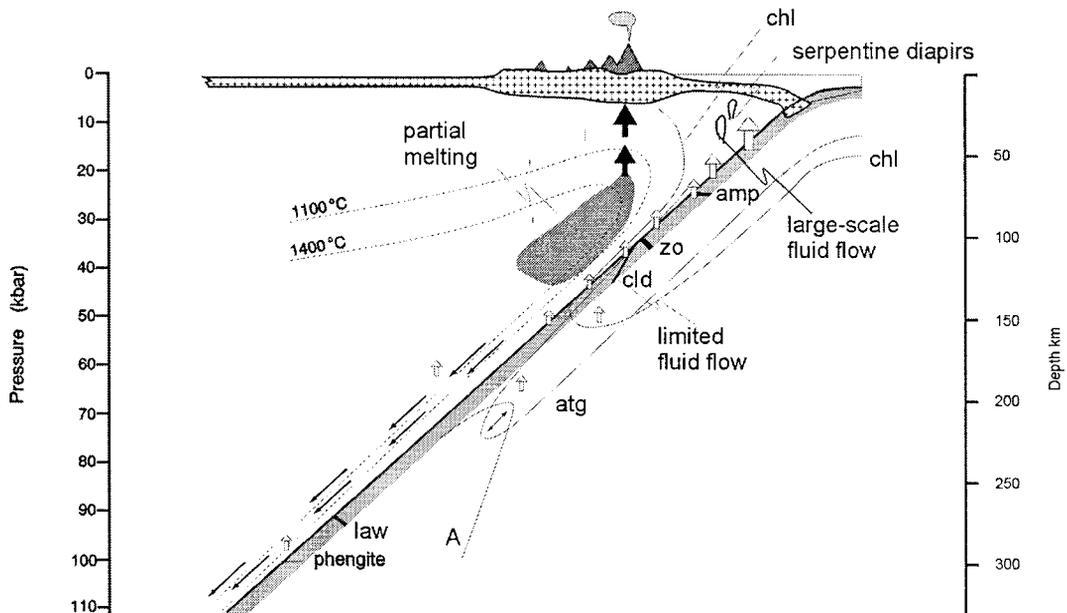


Fig. 4. Model for fluid release from the subducting lithosphere (after Schmidt and Poli, 1998). Dehydration of peridotite and (ideally) overlying mafic crust (grey) occurs continuously down to about 200 km through breakdown reactions of hydrous phases in both mafic (thick solid lines) and ultramafic (light solid lines) slab components. Open arrows indicate rise of fluid, solid ones rise of melts. Large scale and abundant fluid inflow into the mantle of isotopically homogeneous fluids occurs at more surficial levels, whereas limited flow of heterogeneous fluids at local scales is related to deeper subduction environments (Philippot, 1993). Mineral abbreviations: chl = chlorite; amp = amphibole; Zo = zoisite; cld = chloritoid; atg = antigorite; A = phase A; law = lawsonite.

Unfortunately, trace element partitioning between these minerals and coexisting fluids at the pressures and temperatures of subduction is still unexplored.

The highest amounts of subduction water are transported by serpentized ultramafites, where antigorite stores 13 wt.% water at eclogite-facies (Scambelluri et al., 1995). At  $P > 2.5$  GPa, antigorite breakdown to olivine + enstatite represents a major water source for calc-alkaline magmatism (Ulmer and Trommsdorff, 1995). At higher pressures, antigorite breakdown to hydrous phase A + enstatite indicates that water can be transferred deeper than 200 km (Thompson, 1992; Ulmer and Trommsdorff, 1995). Numerous hydrous magnesian silicates have also been described in high- and very-high pressure metasediments (sudoite, Mg-carpholite, Mg-chloritoid, yoderite, ellenbergerite, Mg-stauroilite, K-crymite) (Chopin and Schreyer, 1983; Schreyer and Seifert, 1969; Schreyer, 1988). Most reactions forming these phases are pressure-dependent and water-preserving: accordingly, it has been suggested that during burial of metasediments most dehydration water could be transferred from one hydrous mineral to another (see Philippot, 1993). The stability fields of key hydrous phases in mafic and ultramafic systems reported in Fig. 4 (after Schmidt and Poli, 1998) show that such minerals transport and discharge water directly into the subarc mantle, without needing to bury slices of mantle rocks altered at shallower levels. Most importantly, these hydrous minerals are able to feed off aqueous fluids at much deeper levels of the upper mantle.

### **3. Fluid compositions and densities: the analysis of fluid inclusions**

The occurrence of primary fluid inclusions in rock- and vein-forming eclogitic minerals provides evidence for the ubiquitous presence of fluids during eclogitization of most slab components (sediments, oceanic and continental lithosphere) (Andersen et al., 1989, 1991, 1993; Philippot and Selverstone, 1991; Touret, 1992; Selverstone et al., 1992; Klemd et al., 1992; Giaramita and Sorensen, 1994; Philippot et al., 1995; Scambelluri et al., 1997, 1998; Svendsen et al., 1999). Analysis of fluids in the above settings places constraints on the composition and nature of mobile

phases released at variable depths and their reaction pathways during eclogitization (Philippot and Van Roermund, 1992; Andersen et al., 1993; Scambelluri et al., 1998).

#### *3.1. Fluid inclusions in rock-forming minerals and in shear zones*

These are the least abundant inclusions and form core clusters in rock-forming porphyroblasts and in mineral inclusions armoured by high-pressure crystals. They are interpreted either as exsolution fluids, precipitated from the host during replacement of precursor phases, or as dehydration fluids evolved during early episodes of slab devolatilization (Philippot and Scambelluri, 1996). In the Dora-Maira coesite unit (Western Alps), the ultrahigh pressure assemblage forms by the reaction kyanite + talc = coesite + pyrope + fluid; primary fluid inclusions in relict kyanite represent remnants of prograde dehydration fluid predating crystallization of coesite and pyrope and contain low salinity liquid  $H_2O$  + vapour  $CO_2$  (Philippot et al., 1995). Fluids related to early stages of eclogitization are also preserved in coarse omphacite (less frequently garnet) from eclogites of the Alps (Monviso, Rocciavrè, Voltri and Mt. Emilius; Philippot and Selverstone, 1991; Nadeau et al., 1993; Vallis and Scambelluri, 1996; Scambelluri et al., 1998; Philippot et al., 1998) and of Californian and Dominican blueschist melanges (Giaramita and Sorensen, 1994). These are tubular inclusions whose long dimensions are parallel to the crystallographic faces of omphacite (Fig. 5A); they contain liquid + vapour  $\pm$  solid and are mostly aqueous inclusions with variable amounts of chlorides. Salinity is generally low, but concentrations of 17–21 wt.% and 32–45 wt.% NaCl equivalents have been found, respectively in the Monviso and Rocciavrè matrix inclusions. Similarity in the hydrogen isotope signature of inclusions in Monviso eclogites with that of oceanic chlorite and amphibole from oceanic gabbros has suggested that the Monviso inclusions were produced during dewatering of pre-subduction hydrous phases (Nadeau et al., 1993).

Shear zones are other important rock domains where fluid and deformation channelling facilitate kinetics of the eclogitic mineral reactions. In Norwegian and some Alpine eclogites, fluid-assisted eclogi-

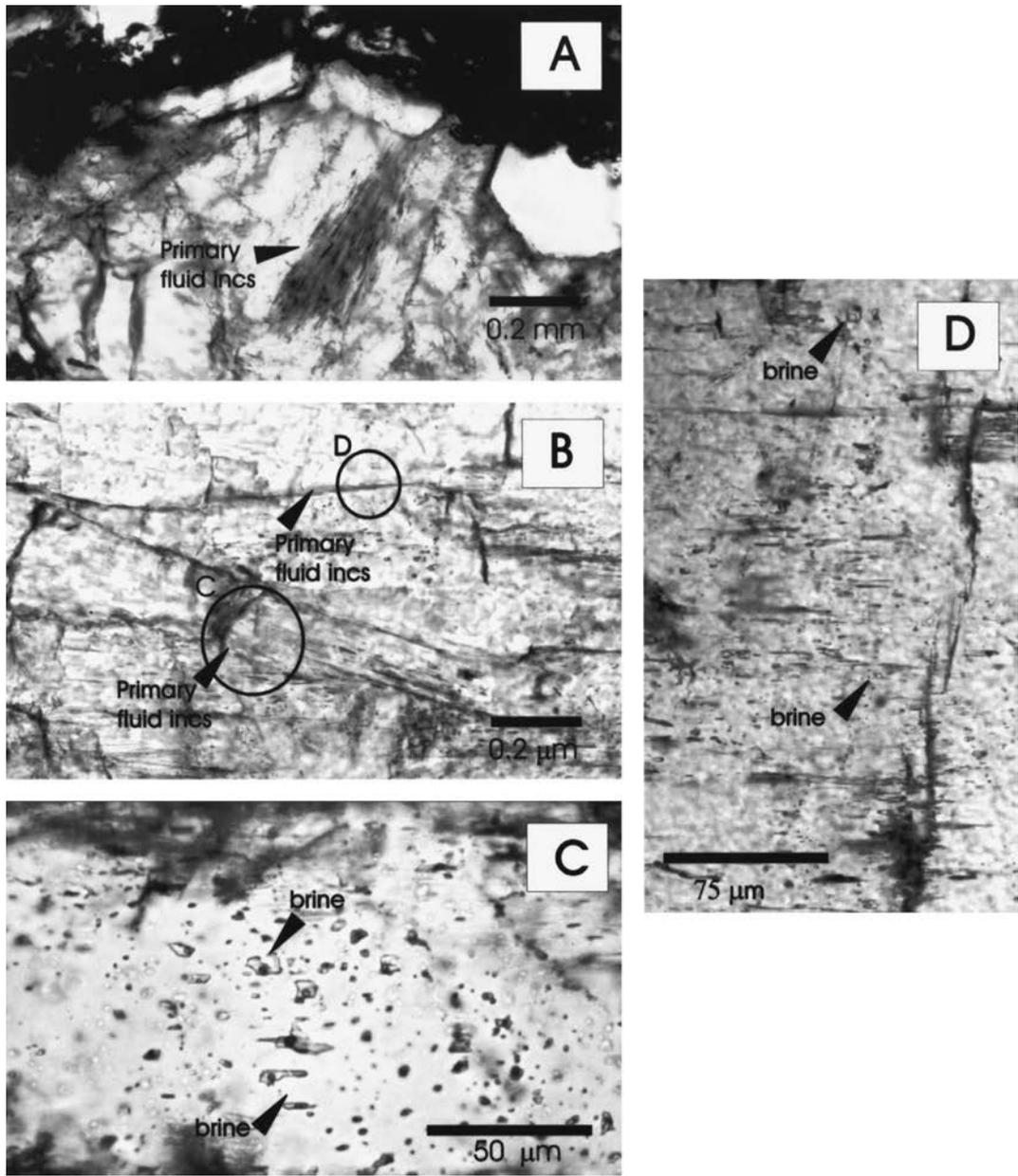


Fig. 5. Micrograph showing fluid inclusion textures in eclogitic rocks. (A) core clusters of fluid inclusions in omphacite porphyroclasts from eclogitic mylonites. (B) omphacite fibres from high-pressure veins in eclogites, showing core cluster of primary fluid inclusion tubes parallel to the stretching direction and to long axes of fibers. (C) primary liquid + vapour and liquid + vapour + halite inclusions in vein omphacite from eclogites.

tization of precursor crustal granulites in correspondence of shear zones (Austrheim, 1987; Pennacchioni, 1996) was accompanied by compositional changes of the associated fluids. In Western Norway,

quartz armoured by coarse eclogitic garnets contains early low-salinity aqueous solutions with  $N_2 + CO_2$  (Andersen et al., 1989). In the Bergen Arcs of Western Norway, in particular, comparable early

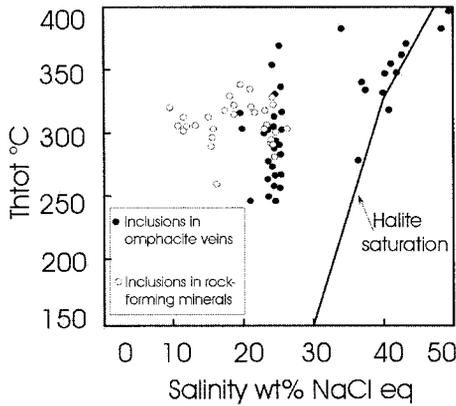


Fig. 6. Compositional variations in primary fluid inclusions inside rock- and vein-forming eclogitic minerals in the Mt. Emilius (Western Alps) crustal granulites eclogitized during alpine subduction (after Scambelluri et al., 1998).

populations of  $H_2O-N_2$  inclusions are postdated by diffuse anhydrous  $CO_2-N_2$  fluids, likely related to more advanced stages of eclogitization and fluid interaction with peraluminous melts infiltrating the shear zones (Andersen et al., 1991, 1993; see below). Highly saline fluid inclusions with up to 18 solid phases (some of which are Pb-bearing) recently found in omphacite from Norwegian eclogites, suggest element fractionation during hydration of the host rocks (Svensen et al., 1999). The above phases, brine and  $CO_2-N_2$  gas, may be related to fluid immiscibility at high-pressure conditions (Andersen, personal communication). In the Alpine Mt. Emilius continental unit, infiltration of aqueous fluid during crystallization of hydrous eclogitic assemblages after precursor dry granulites, was followed by fluid redistribution in high-pressure veins (Pennacchioni, 1996). Primary fluid inclusions in host-rock minerals contain 10 to 25 wt.% NaCl, whereas vein minerals contain 25 to 50 wt.% salts (Fig. 6). Such a salinity change from rock to vein fluids likely reflects water consumption from the fluid during eclogitic hydration of the precursor granulite, thus increasing from 2 to 5 times the chloride contents of residual fluids drained in the veins (Scambelluri et al., 1998).

### 3.2. Fluid inclusions in high-pressure veins

These are the most widespread inclusion types in alpine eclogite-facies rocks. In the Alps, high pres-

sure vein systems formed in eclogites and serpentinites of the subducting oceanic lithosphere, as well as in subducted continental slices. The veins contain the same mineral assemblages as the host rocks, indicating that their filling material is locally derived. Stable C–O–H isotope data (Nadeau et al., 1993; Getty and Selverstone, 1994; Vallis et al., 1997) show that fine-scale heterogeneities were generated during eclogitization and veining. This requires that fluids were internally-buffered by their host rocks and that vein minerals were precipitated from saturated solutions derived from the surrounding rocks. The high-pressure veins display variable textures and contain: (i) blocky minerals with oscillatory zoning and random orientations; (ii) stretched fibre crystals. Fluid inclusions are present in both cases: the growth surfaces of zoned crystals are decorated by primary fluid inclusions and are cut by pseudosecondary inclusion trails; the stretched fibre crystals (mostly clinopyroxene) contain clusters of primary tubular inclusions that parallel the long axis of fibres (Fig. 5B) without cutting the grain boundaries (Philippot and Selverstone, 1991; Scambelluri et al., 1997; 1998). The inclusions contain liquid + vapour  $\pm$  halite  $\pm$  sylvite and correspond to briny aqueous solutions with up to 50 wt.% salts (Fig. 5C, D); presence of additional solid phases indicates that the fluids carried substantial amounts of major and trace elements. A large variety of daughter-mineral suites has been reported in Alpine fluid inclusions: calcite + dolomite + anhydrite + barite + rutile + sphene + baddeleyite + monazite + Fe oxides (Philippot and Selverstone, 1991); carbonates + Fe–Ti oxides + rutile + apatite + mica + zoisite + Ca-sulphates + kyanite + omphacite + glaucophane (Selverstone et al., 1992); quartz (Scambelluri et al., 1998); ilmenite + magnetite (Scambelluri et al., 1997). Some of these solid phases may have formed as a result of interaction between inclusion fluid and host mineral and thus can be considered as “step-daughter crystals” since they contain components from both fluid and host (Heinrich and Gottschalk, 1995).

### 3.3. Fluid–melt–rock interactions

Equilibrium thermodynamics predicts high water activities for eclogitic fluids (Holland, 1979; Jamtveit

et al., 1990). However, water-rich eclogitic fluids are few and restricted to early episodes of rock dewatering and recrystallization. Widespread finding of brines and of anhydrous CO<sub>2</sub>-N<sub>2</sub> inclusions indicates that solute concentration, rather than dilution, occurred during eclogitic fluid–mineral and fluid–melt interactions. In eclogitized mafic granulites of the Alps, fluid–mineral interactions in absence of melt caused large compositional shifts of involved fluids (Fig. 6; Scambelluri et al., 1998). Comparable processes were first documented in Western Norway, where fluid–melt–rock interactions changed the starting compositions of CO<sub>2</sub>- and N<sub>2</sub>-bearing aqueous solutions (Andersen et al., 1991; 1993). H<sub>2</sub>O was consumed in the production of amphibole, zoisite and mica, and also partitioned in the melt phase; these processes left behind residual solutions enriched in CO<sub>2</sub> and N<sub>2</sub>. Moreover, CO<sub>2</sub> was leached from granulite-facies inclusions in the host rocks and N<sub>2</sub>, fixed in ammonium-bearing minerals, became soluble in low a<sub>H<sub>2</sub>O</sub> residual fluids (Andersen et al., 1993). The sum of these interactions led to a change of the initial fluid compositions and to formation of anhydrous CO<sub>2</sub> and N<sub>2</sub>-rich solutions (Andersen et al., 1993). Significant changes in fluid composition in response to fluid–melt interactions were also proposed for the Alpine Dora Maira unit (Sharp et al., 1993; Philippot et al., 1995). Sharp et al. (1993) showed that pyrope + coesite (700–750°C, *P* > 3.0 GPa) cannot form in these rocks unless the water activity was reduced to 0.4–0.7. They proposed that H<sub>2</sub>O partitioning into coexisting melts decreased the water activity in the residual fluid. Evidence of very high-pressure melts is represented by jadeite–coesite quartzite layers closely associated with the pyrope–coesite quartzite (see Sharp et al., 1993 for discussion). Philippot et al. (1995) recognized that interaction of early dehydration aqueous fluids (still preserved in kyanite relics within pyrope) with the melt was accompanied by fluid partitioning in two phases: (i) a water-rich Na, Ca, Mn, Cu, Zn, Cl fluid, found in secondary inclusions in the jadeite–coesite quartzite, representing the melt phase; (ii) a residual Mg-rich aqueous-carbonic fluid found in decrepitated inclusions in pyrope. Water partitioning into the melt, thus left a carbonic residue in the coesite–pyrope schist, due to much lower solubility of CO<sub>2</sub> in melt. Importantly, fluid–melt interactions during

exhumation again controlled the fluid composition: melt crystallization exsolved high-pressure hypersaline fluids that infiltrated the pyrope–coesite rocks and caused retrograde breakdown of garnet (Philippot et al., 1995).

These examples show how rocks and melts can buffer, change and even reverse the initial compositions of subduction fluids. The ultimate compositions they achieve thus reflect (and depend on) the type of interactions experienced during their flow pathways inside the slab. The effects of such interactions on trace element redistribution are difficult to quantify and are not investigated in detail. Therefore, modeling the compositions of fluids that exit the slab necessarily requires much deeper understanding of the interaction processes that fluids experience during their slab history.

### 3.4. Fluid inclusion densities

Despite textural evidence that fluid inclusion entrapment in many eclogite–facies rocks occurred at high and very high pressures, the pressure–temperature values obtained from fluid inclusion isochores generally underestimate the peak metamorphic conditions achieved from mineral thermobarometry. In many cases, in fact the densities of primary inclusions in high-pressure omphacite, garnet and quartz are much lower than expected: the corresponding isochores generally plot several kilobars below the eclogitic estimates (Klemd, 1989; Philippot and Selverstone, 1991; Selverstone et al., 1992; Giaramita and Sorensen, 1994; Scambelluri et al., 1998) and correlate only rarely with peak pressures and temperatures. In the eclogite–facies metasediments of the Munchberg gneiss complex, Klemd et al. (1992) showed that small (< 8 μ) CO<sub>2</sub>-N<sub>2</sub> inclusions still preserve high densities, compatible with the eclogitic mineral thermobarometry; however, the majority of primary CO<sub>2</sub>-N<sub>2</sub> inclusions have much lower densities and were affected by a density reset at amphibolite-facies. Density reequilibration of fluid inclusions during exhumation thus appears dependent on the geometry and size of the inclusion, small fluid inclusions being able to hold higher internal pressures than larger ones (Bodnar et al., 1989). Although density changes involve the great majority of fluid inclusions, the original fluid compositions

can survive the reequilibration processes. An experimental study on synthetic  $\text{H}_2\text{O}$ – $\text{NaCl}$  inclusions (Sterner and Bodnar, 1989) shows that although density reset occur during burial and exhumation, the original fluid compositions can be preserved. These features indicate that eclogitic inclusions in rock- and vein-forming minerals can still provide direct evidence for the nature and compositions of the subduction fluids, despite necking down, partial decrepitation and stretching have modified the inclusion densities during their pathway towards the Earth's surface. In some cases, fluid inclusion reequilibration is associated with the metamorphic recrystallization of host mineral phases. Vallis and Scambelluri (1996) have shown that reequilibration of primary inclusions in omphacite of alpine eclogites enhanced recrystallization of the host sodic clinopyroxene into plagioclase + diopside  $\pm$  amphibole. Survival and preservation of eclogitic fluids thus necessarily requires unfavourable reaction kinetics during overall retrograde metamorphism and readjustment of the fluid inclusion densities.

As discussed by Philippot and Selverstone (1991), the difficulty of obtaining peak pressures from fluid inclusion isochores can also be due to the lack of  $P$ – $V$ – $T$  data for complex fluids, and to the difficulty of estimating the volumes of liquid, vapor and daughter phases in inclusions which are very small (about 10  $\mu\text{m}$ ) and often irregular in shape. As discussed above many primary inclusions in eclogitic rocks and veins can display several daughter phases such as chlorides, silicates and oxides (Philippot and Selverstone, 1991; Selverstone et al., 1992; Scambelluri et al., 1997; Svensen et al., 1999). Due to the lack of appropriate  $P$ – $V$ – $T$  data on such complex solutions, evaluation of the inclusion densities is impossible. As a consequence, the large pressure mismatch obtained comparing fluid isochores and mineral termobarometry can be the result of both complex fluid compositions and the effect of density reequilibration of the inclusion fluids.

#### 4. Experimental constraints on the compositions of subduction fluids

The question of the nature and compositions of subduction fluids remains a crucial point of contro-

versy, since quantitative assessment of their major and trace element contents is hampered by paucity of information on mineral solubilities and on mineral–fluid partitioning of trace elements at high pressures and temperatures. Based on mineral–solution equilibria in mafic and metasedimentary systems at 400–600°C and 1.0–2.0 GPa, Manning (1996; 1998) has shown that  $\text{SiO}_2$  solubility increases with pressure and temperature. In metasediments, above 1.2 GPa and 550°C, its concentration rises to  $> 2$  wt.% ( $10^{-0.5}$  molal); in mafic systems, aqueous fluids with 1 molal Cl (6 wt.% NaCl equivalent) can dissolve equal amounts of  $\text{Na}_{\text{aq}}$  and  $\text{SiO}_{2\text{aq}}$  ( $10^{-0.5}$  m, about 2 wt.%), and much lower  $\text{Al}_{\text{aq}}$  ( $10^{-2}$ – $10^{-3}$  m, 1–0.1 wt.%) and  $\text{Mg}_{\text{aq}}$  ( $10^{-7}$  m). Comparably low solubilities were reported by Schneider and Eggler (1986) for ultramafic systems. In contrast, other studies point to much higher mineral solubilities in high-pressure fluids (Ryabchikov and Boettcher, 1980; Ryabchikov et al., 1982; Ryabchikov, 1993; Massonne, 1992; Domanik and Holloway, 1998). According to Massonne (1992), solubility of metasedimentary rocks (2 micas, K-feldspar, quartz) in aqueous fluids at 2.0 GPa and 550°C may be as high as 50 wt.%. Comparable concentrations of silicate-component can be dissolved in fluids in equilibrium with lherzolite at 150 km depth (Ryabchikov, 1993). Recent experiments by Domanik and Holloway (1998) show that fluids produced during recrystallization of calcareous metapelite at 6.5–11 GPa and 750–1050°C contain approximately 40 mol% solute at 8 GPa and 60 mol% at 11 GPa. These experiments thus suggest that high pressure fluids can be characterized by high solute concentrations. Additional experimental data at high pressures and under controlled pH, oxygen fugacity and Cl activity are urgently needed to provide better constraints on possible fluid compositions at great depth. At this stage, however, note that high Si, Na, Al concentrations in eclogitic fluids can explain the presence of omphacite–quartz and quartz–kyanite segregation in eclogite–facies rocks (Philippot, 1996; Manning, 1998), as well as precipitation of quartz daughter crystals during cooling of fluid inclusions trapped in vein omphacites (Scambelluri et al., 1998).

Recently, experiments at high  $P$ – $T$  have also been performed to determine the partitioning be-

haviour of HFSE between minerals and aqueous solutions with variable concentrations of salts and solute, but the results are sometimes contrasting (compare the different results of Keppler, 1996; Brenan et al., 1995; Stalder et al., 1998), probably due to different experimental strategies and materials employed. Measurements of low rutile solubilities in aqueous fluids (Ayers and Watson, 1993), combined with high rutile-fluid partition coefficients of HFSE [ $D^{\text{rutile-fluid}}$  147 (Nb); 147 (Ta), 94 (Hf), 206 (Zr); Brenan et al., 1994], suggest that rutile stability in eclogitic assemblages causes selective HFSE-depletion of released fluids. A comparable role may be played by other Ti-bearing minerals like ilmenite and Ti-clinohumite (Ayers et al., 1997; Scambelluri et al., 2000). Brenan et al. (1995) and Stalder et al. (1998) determined that rutile-free garnet + clinopyroxene + amphibole assemblages do not cause significant HFSE depletion in the coexisting aqueous fluid, and that rutile plays the main role in depleting the slab fluids of such elements. However, the occurrence in nature of rutile and other Ti- and HFSE-bearing phases (ilmenite, Fe-Ti oxides, Ti-clinohumite) as vein minerals and as solid phases in fluid inclusions, provides compelling evidence that these minerals at a certain stage became soluble and that Ti plus other HFSE were transported by the eclogitic fluids. Moreover, close correspondence between rock and vein mineralogies indicates that fluids were solute-rich and saturated with host-rock components. The natural observations thus give credit to experimental results indicating high solubilities and elevated solute concentrations in high-pressure fluids. Deep subduction fluids may thus correspond to silicate-rich soups, with water as the main solvent. Brenan et al. (1995) showed that addition of NaCl and solute to fluids lowers the trace element mineral/fluid partition coefficients, thereby increasing the trace element solubility in the fluid. At sufficiently high solute concentrations (7–10 wt.% according to Brenan et al., 1995), fluids approach the transport capacity of melts and the two metasomatic agents become difficult to distinguish.

## 5. Origin of subduction fluids and chlorine

Island arc magmas display much higher Cl concentrations (460–2000 ppm, see Fig. 2A) than mag-

mas from other tectonic settings (Perfit et al., 1980). Presence of highly to moderately saline inclusions in eclogite-facies rocks suggests that these chlorine-bearing fluids were involved in the overall transfer process. Assessing the timing of infiltration of the Cl-fluids and the scales of fluid motion in high-pressure rocks adds important constraints to processes of fluid migration in deep regions of subducting slabs, and on volatile cycling during subduction.

Although several studies show that externally-derived fluids do infiltrate rocks during eclogitization (Austrheim, 1987; Andersen et al., 1993; Rubie, 1990; Scambelluri et al., 1998), growing evidence indicates that in many instances eclogitic fluids are internally cycled and that their uptake predates subduction and high-pressure metamorphism (Matthews and Schliestedt, 1984; Pognante, 1985; Messiga and Scambelluri, 1989). Despite release of devolatilization fluids, preservation of fine-scale oxygen isotope heterogeneities in many eclogite-facies rocks indicates only limited fluid-rock exchange, thereby suggesting short-range fluid mobility and redistribution of limited packages of fluids into veins during eclogitization (Matthews and Schliestedt, 1984; Nadeau et al., 1993; Getty and Selverstone, 1994; Frueh-Green, 1994; Yui et al., 1995; Barnicoat and Cartwright, 1997; Baker et al., 1997; Vallis et al., 1997). Preservation of pre-subduction oceanic isotopic signatures in some rocks indicates that internal cycling of ocean water, rather than infiltration of external fluid occurred during eclogitization (Matthews and Schliestedt, 1984; Nadeau et al., 1993; Barnicoat and Cartwright, 1997; Philippot et al., 1998). Deep cycling of seawater-derived fluids has been also recognized in subducted ultramafic rocks, where breakdown of oceanic Cl- and alkali-bearing hydrous phases is accompanied by partitioning of these components into a high-pressure alkaline brine (Scambelluri et al., 1997).

Philippot et al. (1998) recently compared the oxygen isotope and fluid inclusion data available for oceanic and ophiolitic rocks with those of their eclogitized equivalents (Fig. 7). Rocks at surficial levels of the oceanic lithosphere undergo complex low-temperature alteration, that ultimately results in  $\delta^{18}\text{O}$ -enriched signatures (Gregory and Taylor, 1981). On the other hand, deep oceanic gabbros are  $\delta^{18}\text{O}$  depleted during high-temperature alteration associ-

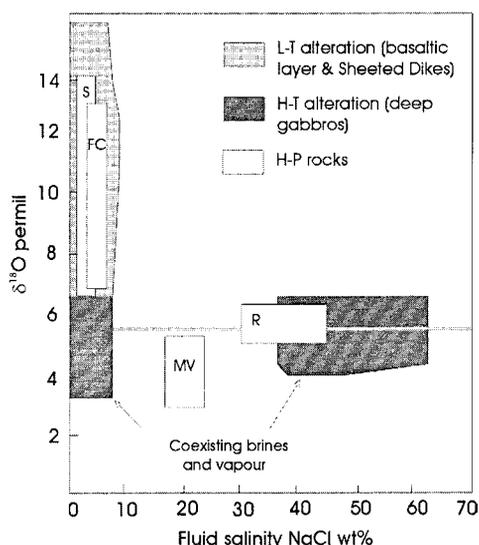


Fig. 7. Fluid inclusion salinities versus  $\delta^{18}\text{O}_{(\text{whole rock})}$  or  $\delta^{18}\text{O}_{(\text{omphacite})}$  in oceanic rocks which underwent high- and low temperature alterations, and in their high-pressure counterparts. Oceanic rocks are both from mid-ocean ridges (Kane fracture zone and Holes 504B, 735B), and from Semail and Troodos ophiolites (data sources in Philippot et al., 1998). The high-pressure rocks (white boxes) are from the Franciscan Complex (FC; North America), Sifnos (S; Greece), Monviso and Rocciavre (MV and R; Western Alps) (data sources in Philippot et al., 1998).

ated with briny fluids and formation of Cl-rich amphiboles. The variable  $^{18}\text{O}$  signatures and salinities of fluids of high-pressure rocks may reflect alteration at different levels of the oceanic lithosphere. The  $\delta^{18}\text{O}$ -enriched eclogites of Fig. 7 likely derive from materials originally located at high crustal levels of the oceanic lithosphere: they still preserve a stable isotope imprint acquired during low-temperature oceanic alteration and contain primary inclusions whose low-salinities compare well with inclusions in oceanic rocks altered at low temperatures (Matthews and Schliestedt, 1984; Philippot et al., 1998). In contrast, the eclogitic metagabbros of Fig. 7 have  $\delta^{18}\text{O}$  depleted signatures and high fluid inclusion salinities that are very similar to those of oceanic gabbros altered at high temperatures. These systematic similarities in inclusion fluid and  $\delta^{18}\text{O}$  compositions imply that subduction did not significantly modify the chlorinity and oxygen isotope signatures of altered oceanic precursors. High-pressure rocks thus appear to behave as grossly closed systems that

internally cycle their own fluids and elements; this indicates that oceans are the primary sources of water and chlorine cycled in deep subduction fluids. Using these eclogite-facies rocks as tracers to estimate the net amount of chlorine transferred from oceans to the mantle, Philippot et al. (1998) estimated that 100–200 ppm Cl per unit volume are returned to the deep mantle during subduction. This yields a Cl/ $\text{H}_2\text{O}$  ratio of  $3.6\text{--}7.5 \times 10^{-2}$ , which is similar to E-MORB ratio.

## 6. Fluid migration mechanisms

Fluid inclusion studies suggest that devolatilization of subducting slabs mostly evolves aqueous solutions. Diffuse arc volcanism and finding of aqueous silicate melts and/or water-rich fluids only in peridotite xenoliths from mantle regions above subduction settings (Schiano et al., 1995; Andersen and Neumann, 2001) implies fluid transfer from the slab to the overlying mantle wedge. On the other hand, with the exception of cases where fluid infiltration drives the eclogitization of anhydrous protoliths (Norwegian Caledonides and Mt. Emilius), the eclogite-facies rocks equilibrated between 40 and 120 km do not appear to record fluid motions over large scales. There is therefore an apparent controversy between the evidence of limited fluid flow in eclogitic rocks and the requirement that fluids move from the subducting slab into the mantle. This contradiction can be explained by proposing that the exhumed high-pressure rocks do not represent the levels where fluids are extracted from the slab. Fluids mostly remain entrapped in the slab and are injected into the upper mantle at depths greater than those attained by most exposed eclogites; higher pressure rocks need thus to be exhumed (or found) in order to find the regions of important fluid loss from the slab. Antigorite, for instance, is stable in alpine serpentinites subducted to 2–2.5 GPa and to the quartz-coesite transitions (Scambelluri et al., 1995): its breakdown at greater depth and temperature would liberate large amounts of fluid and induce deep earthquakes and fracturing (Reinen et al., 1998). Such processes could enable fluid channelling and motion over appreciable scales throughout the slab. Also, Watson et al. (1993) showed that in mantle

materials transition from immobile (isolated pockets) to mobile fluids (interconnected along grain edges) is related to decrease of wetting (dihedral) angles  $\theta$  between fluid and mineral interfaces below a critical value of  $60^\circ$  (mobile fluids having  $\theta < 60^\circ$ ). Decrease of  $\theta$  occurs at increasing pressure and temperature: in particular, aqueous fluids may form an interconnected phase at about 3 GPa and  $T$  close to solidus. These general features may suggest a depth-related change in fluid mobility with ongoing subduction.

## 7. Conclusions

Fluid inclusion systematics indicate fluid–melt–rock interactions controlled the major element and volatile compositions of ambient fluids. Trace element fractionation during such interactions need to be deeper tested and quantified to achieve the ultimate compositions attained by fluids leaving off the slab. Fluid inclusion studies moreover indicate that subduction of mature oceanic crust is mainly accompanied by production of aqueous fluids, melts being produced only locally. Variably saline inclusions with minor  $\text{CO}_2$  and  $\text{N}_2$  are trapped in rock-forming minerals, and brines with up to 50% weight dissolved solute are diffusely trapped in veins. The latter inclusions are residues after fluid–rock interactions and deposition of complex vein mineralogies: this evidence suggests that at a certain stage fluids correspond to silicate-rich aqueous solutions whose geochemical behaviour and transport capacity can approach that of a melt phase. This seems supported by experimental work showing solubility of silicate components in fluids at high pressures. However, natural examples of inclusions trapping such a fluid and quantitative analyses of its major and trace element composition are not yet available.

Fluids in high and very high pressure rocks do not move over large scales and the channelways of fluid escape from the slab are not yet identified. This suggests that only part of the slab fluid evolved is lost and returned to the surface via magmatism; the remaining trapped fraction being subducted into deeper levels of the upper mantle, to renew its budget of substances initially stored in the exosphere.

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