Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction zones

Jörg Hermann [a,*], Carl Spandler [a], Alistair Hack [a,1], Andrey V. Korsakov [b]

[a] Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia
[b] Institute of Mineralogy and Petrography of Siberian Branch of Russian Academy of Sciences, Koptyug Pr. 3, Novosibirsk 630090, Russia

Abstract

High-pressure (HP) and ultra-high pressure (UHP) terranes are excellent natural laboratories to study subduction-zone processes. In this paper we give a brief theoretical background and we review experimental data and observations in natural rocks that constrain the nature and composition of the fluid phase present in HP and UHP rocks. We argue that a fluid buffered by a solid residue is compositionally well defined and is either an aqueous fluid (total amount of dissolved solids < 30 wt.%) or a hydrous melt (H_2O < 35 wt.%). There is only a small temperature range of approximately 50–100 °C, where transitional solute-rich fluids exist. A review of available experimental data suggest that in felsic rocks the second critical endpoint is situated at 25–35 kbar and ∼ 700 °C and hence must be considered in the study of UHP rocks. Despite this, the nature of the fluid phase can be constrained by relating the peak metamorphic conditions of rocks to the position of the wet solidus even if the peak pressure exceeds the pressure where the wet solidus terminates at the second critical endpoint. Transitional solute-rich fluids are expected in UHP terrains (P > 30 kbar) with peak temperatures of about 700 ± 50 °C. At higher temperatures, hydrous granitic melts occur whereas at lower temperatures aqueous fluids coexists with eclogite-facies minerals. This argument is complemented by evidence on the nature of the fluid phase from high-pressure terrains. We show that in the diamond-bearing, high-temperature UHP rocks from the Kokchetav Massif there are not only hydrous felsic melts, but probably also carbonate and sulfide melts present.

Hydrous quartzo-feldspathic melts are mainly produced in high temperature UHP rocks and their composition is relatively well constrained from experiments and natural rocks. In contrast, constraining the composition of aqueous fluids is more problematic. The combined evidence from experiments and natural rocks indicates that aqueous fluids liberated at the blueschist to eclogite facies transition are dilute. They contain only moderate amounts of LILE, Sr and Pb and do not transport significant amounts of key trace elements such as LREE, U and Th. This indicates that there is a decoupling of water and trace element release in subducted oceanic crust and that aqueous fluids are unable to enrich the mantle wedge significantly. Instead we propose that fluid-present melting in the sediments on top of the slab is required to transfer significant amounts of trace elements from the slab to the mantle wedge. For such a process to be efficient, top slab temperature must be at least 700–750 °C at sub-arc depth. Slab melting is likely to be triggered by fluids that derive from dehydration of mafic and ultramafic rocks in colder (deeper) portions of the slab.
© 2006 Elsevier B.V. All rights reserved.

---

* Corresponding author. Tel.: +61 2 6125 8842; fax: +61 2 6125 5989.
  E-mail address: joerg.hermann@anu.edu.au (J. Hermann).
[1] Present address: Institute for Mineralogy and Petrography, ETH-Zürich, 8092 Zürich, Switzerland.

1. Introduction

It is widely accepted that a fluid phase released from the subducted slab fluxes partial melting in the mantle wedge. Moreover, this fluid phase is responsible for transferring some incompatible elements from the subducted crust through subduction-zone magmatism to newly formed continental crust in arcs (Tatsumi and Eggins, 1995). This recycling of elements through convergent plate boundaries strongly influences the chemical differentiation of Earth. Exhumed high-pressure and ultra-high pressure rocks provide an excellent natural laboratory to study subduction zone processes. The high-pressure, relatively low-temperature metamorphic conditions are similar to what is expected to occur in deeply subducted crust. UHP-rocks are an especially exciting field of research because they enable us to study processes occurring at 100–150 km depths, conditions corresponding to the depths of the subducted slab below volcanic arcs. Fluids play a key role in formation and preservation of HP and UHP rocks. It has been demonstrated that in the absence of fluids, granites and granulites formed at normal crustal pressures do not convert to eclogites even at pressures corresponding to 100 km depth (Austrheim, 1987; Compagnoni et al., 1995). Accordingly, the absence of fluids is a prerequisite to prevent retrograde transformation of UHP rocks during their way back to the surface (Heinrich, 1982). However, even well preserved HP and UHP rocks do not contain a complete record of the composition and physical property of the fluid phase. To characterise the fluid phase present at such extreme metamorphic conditions it is necessary to link observations from natural rocks with experimental and theoretical constraints.

Normal crustal metamorphism occurs in a $P–T$ range where there is a clear distinction between aqueous fluid and hydrous melt. However, in UHP crustal rocks such distinction may not be possible, because at such conditions there is potentially a complete miscibility between aqueous fluids and hydrous melts. The existence of a second endpoint, where the wet solidus terminates, was postulated from theoretical considerations made more than 40 years ago (Wyllie and Tuttle, 1960; Boettcher and Wyllie, 1969), but there has been limited application because at that time UHP metamorphism was not known. With the discovery of UHP metamorphism and new experimental techniques to constrain this complete miscibility in complex systems (Shen and Keppler, 1997; Bureau and Keppler, 1999; Stalder et al., 2000, Kessel et al., 2005a), it became evident that the second critical endpoint needs to be taken into consideration. This has caused a lot of confusion regarding appropriate terminology for the fluid phase in HP and UHP rocks.

In this paper, we first address the problem of fluid terminology at HP and UHP conditions with some considerations of phase relations in hydrous systems. We will review constraints from selected natural rocks and experimental studies and also present some new data in order to characterise the fluid phase present at such extreme metamorphic conditions. We will show that the amount of solutes in the fluid phase can drastically increase over a relatively small temperature interval and discuss implications on phase diagram calculations. Also, we highlight the benefit of using a combined approach of natural and experimental data to constrain fluid-mediated element transfer in subduction zones.

2. Theoretical background

Basic phase relations have been experimentally determined for most silicate–H_2O systems of geological relevance. Conspicuously, the same features are generally observed in both simple and more complex rock–H_2O systems. Fig. 1 schematically depicts the $P–T–X_{fluid}$ relations common to most rock–H_2O systems. This diagram is heavily based on quartz solubility in the simple SiO_2–H_2O system which varies systematically as a function of pressure and temperature (Kennedy et al., 1962; Nakamura, 1974; Manning, 1994). SiO_2–H_2O can be considered as a first order approximation of crustal rocks and a guide to the general behaviour of other complex rock types. Points to note from Fig. 1 are that the addition of H_2O to anhydrous systems significantly lowers melting temperatures, giving rise to the so-called wet solidus, which is also commonly called the vapor- or fluid-saturated melting curve. At high pressure the wet solidus terminates at a position known as the second critical endpoint ($CP^2_{Rock–H_2O}$) and marks the condition where hydrous melt and aqueous fluid become completely miscible on the wet solidus. The occurrence of fluid–melt miscibility at $CP^2_{Rock–H_2O}$ is a critical phenomenon entirely analogous to that observed at the termination of the univariant curve, mineral+aqueous liquid+aqueous vapor, at lower pressure and temperature ($CP^1_{H_2O}$). A critical curve, representing the trace of the apex of the melt+fluid solvus on the $P–T$ plane, links $CP^2_{Rock–H_2O}$ to the critical point of the anhydrous system (CP^3_{Rock}) and represents the upper limit to the aqueous fluid+hydrous melt field. The region and curve where two fluids (or more) are stable are referred to as subcritical, whereas those where only a single fluid phase (hydrous melt or aqueous fluid) is stable is referred to as supercritical.

The term "supercritical fluid" is a source of considerable confusion. Largely this is because the term supercritical merely indicates that a single continuous
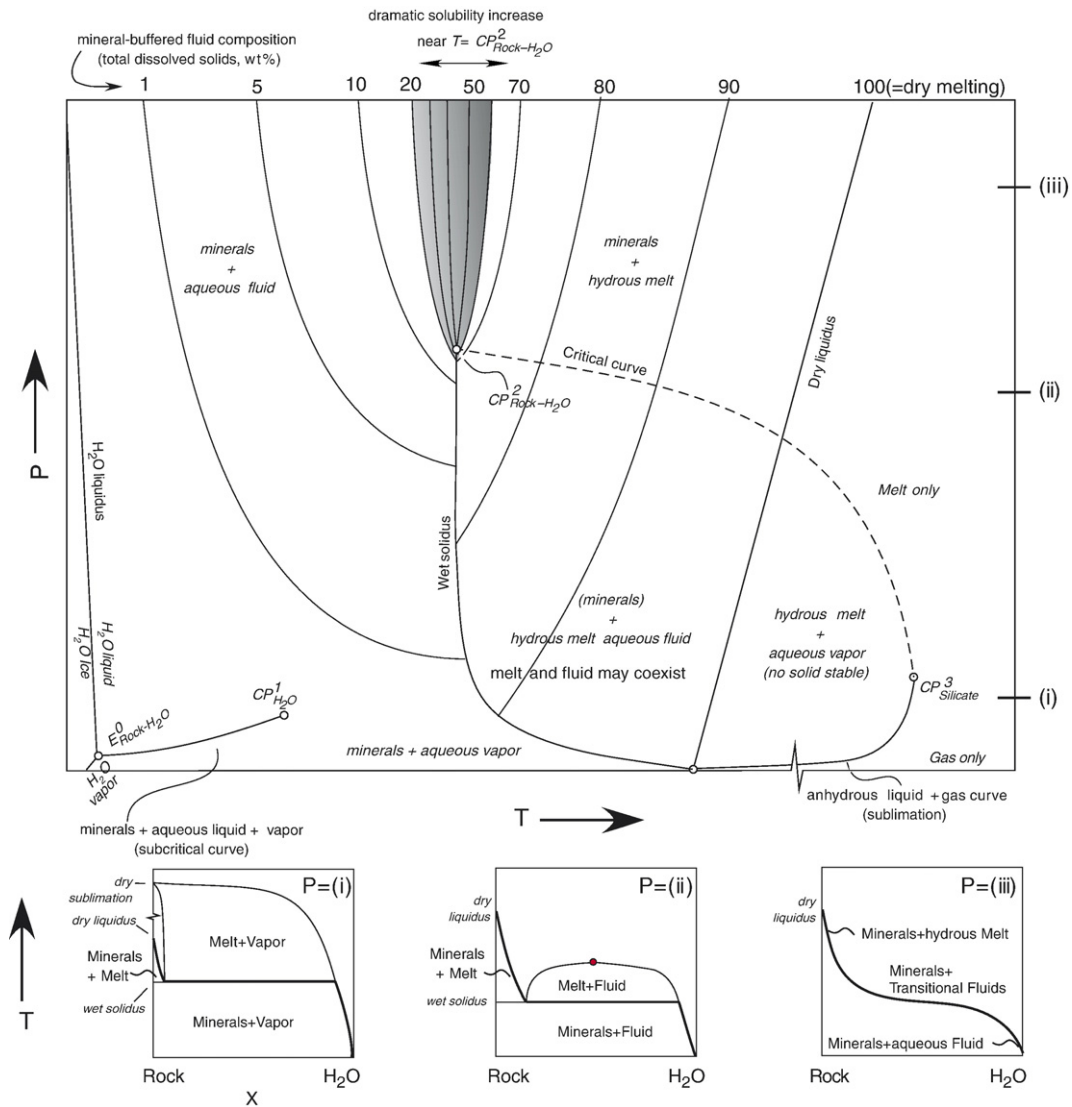
Fig. 1. P–T phase diagram for a simple binary system, rock-H_2O. Also shown are a series of isobaric T–X_{fluid} sections through the P–T projection, at the pressures indicated (i, ii, iii). $E_{Rock-H_2O}^0$ refers to the eutectic point and CP_{syst}^n refers to various critical points (open circles) where n is used to distinguish multiple CP present in the binary system. Phase boundaries are labelled. Stable assemblages in each part of the figure are indicated. Mineral-buffered fluid composition is contoured in weight total dissolved solids. The P–T–X behavior of mineral solubility surface and relative positions of other features mimics that observed for the SiO_2–H_2O system. The rapid change in solubility with temperature near $CP_{Rock-H_2O}^2$ gives rise to two P–T regions in which the compositional characters of mineral-buffered supercritical fluids are distinctly different and is the source for the descriptive supercritical fluid nomenclature used, i.e. aqueous fluid and hydrous melt. The use of such terminology for the supercritical phase does not imply there is a phase transition, sensu stricto, between regions.

solution in the phase of interest (solid or liquid) is stable; it implies nothing about the actual composition at a given pressure and temperature. However, in buffered systems fluid composition is determined by other factors. From a geological perspective it should be noted that fluids and melts, despite their fugitive nature, occur under mineral-saturated conditions and, from thermodynamics, that the composition of all phases are fixed in a buffered system at a given pressure and temperature. Thus, like co-existing mineral compositions, buffered fluid composi-

tions vary systematically as a function of P and T. Accordingly, specific P–T regions can be identified where fluids will have low total dissolved solids and where solubilities are likely to be sufficiently high that they resemble hydrous melts. Hence, specifying the compositional nature of a given supercritical fluid (e.g. supercritical aqueous fluid or supercritical hydrous melt) also indicates a specific P–T region, intended or not. The fluids are supercritical over the majority of the P–T space, not just above $CP_{Rock-H_2O}^2$.

In summary, mineral solubility data for simple systems like SiO_2–H_2O suggest there is a simple and predictable general relation between the temperature at which the wet solidus ends and whether a mineral-buffered supercritical fluid is dilute and H_2O-rich or is solute-rich with a hydrous melt-like composition. Specifically, mineral solubilities increase rapidly with increasing temperature near $T_{CP^2_{Rock–H_2O}}$, such aqueous fluid composition and melt compositions are confined to $T < T_{CP^2_{Rock–H_2O}}$ and $T > T_{CP^2_{Rock–H_2O}}$, respectively. Intermediate fluid–melt compositions are likely to be of minor significance as they are expected to occur only in a very narrow T interval near $T_{CP^2_{Rock–H_2O}}$ (± ~50 °C) and hence are likely to be relatively rare or short-lived (Manning, 2004). Thus, first order compositional information for a fluid (dilute vs. melt-like), which coexisted with a given rock, can be obtained by comparing the P–T conditions preserved within the rock with the position of its wet solidus and $CP^2_{Rock–H_2O}$. The wet solidus and critical curve positions are dependent on bulk rock composition and hence occur at different P and T in different systems.

3. Experimental constraints

The temperatures reached in HP and UHP terranes are situated at the lower end of what can be reproduced in experimental studies. Additionally, the investigated systems are often chemically complex containing phases that are solid solutions between a series of end-members. Such a situation makes it difficult to investigate phase relations and compositions with reversed experiments, the most rigorous approach. Instead, more commonly synthesis experiments are used. For the study of fluid phases at such conditions, as summarised in this work, synthesis experiments seem appropriate because the large amount of fluid present in such experiments catalyses reactions and enhances attainment of equilibrium.

3.1. Phase relations

Experiments are crucial to constrain the position of the wet solidus and the second critical endpoint. Such studies then provide a robust basis for the interpretation of the nature of the fluid phase in HP and UHP rocks. We use the granite + H_2O system to illustrate how these features can be constrained (Fig. 2a). At low pressures, the determination of the wet solidus is straightforward. The presence of melt is clearly documented by glass in experimental runs, whereas below the solidus no glass is present. With increasing pressure along the wet solidus, the water content in the melt increases (Huang and Wyllie, 1981; Holtz et al., 2001). This causes considerable complication. A melt with about 30–40 wt.% H_2O does not quench any more to a glass but to a solute-rich hydrous quench material. Hence the distinction between "glass present" and "glass absent", which was used to determine the position of the solidus, might represent a solubility isopleth rather then the real wet solidus (Fig. 2a). Classical wet-melting studies in natural rock compositions did not find a second critical endpoint, which might be due to the fact that most piston cylinder studies were limited to a pressure up to 35 kbar (Lambert and Wyllie, 1972; Huang and Wyllie, 1981). It is worth noting that these studies mention that distinction between fluid-quench and glass is difficult at 35 kbar. The position of the second critical endpoint can only be constrained when solubilities in the fluid phase are considered. This is experimentally very challenging and so far only a few studies exist. For the granitic system, Bureau and Keppler (1999) performed diamond anvil experiments where they were able to directly observe the transition from aqueous fluid + hydrous melt to one single fluid as a function of pressure and temperature. Although the data set does not cover the full range of temperatures down to the wet solidus, the extrapolation of the data suggest that the critical point is situated at about 25–30 kbar (Fig. 2a). Schmidt et al. (2004) proposed a second critical endpoint in pelitic to greywacke compositions at considerable higher P–T conditions (Fig. 2b) that seems inconsistent with the observed trend lines of direct miscibility reported by Bureau and Keppler (1999). Also, experiments in pelitic systems (Hermann, unpublished data) display clear evidence of melting at 800 °C in the pressure range of 25–45 kbar, which does not support a strong backbend in the solidus. A different approach to determine solubility close to the second critical endpoint has been by capturing the fluid phase in a diamond trap, which then is analysed by Laser Ablation ICP-MS. This approach is very promising as it can be applied over a large range of P–T conditions. Stalder et al. (2000) successfully mapped out the albite + H_2O second critical point at about 16 kbar, 700 °C with this method. Kessel et al. (2005a) investigated the basalt + H_2O system at 40–60 kbar and 700–1400 °C to characterise fluid compositions. Their data suggest that the second critical point in such a K-free system is situated at 50–60 kbar. The wet solidus deduced from solubility data from the diamond traps is placed at 850–900 °C at 40 kbar and approaches the wet solidus of peridotites at 50 kbar (Fig. 2b). This strong bend in the solidus leads to a 100 °C higher temperature of the solidus at 35 kbar with respect to the solidus determined by Lambert and Wyllie (1972). For the peridotite + H_2O system there is
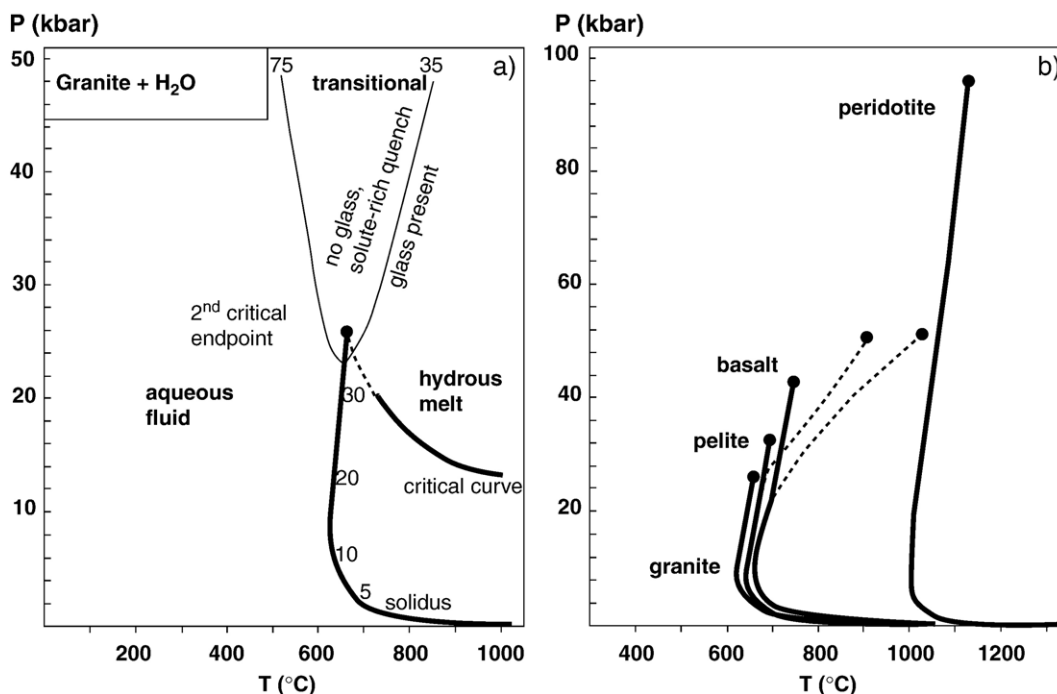
Fig. 2. The position of the second critical endpoint in the system granite+H$_2$O (a). The position of the wet solidus (Huang and Wyllie, 1981; Holtz et al., 2001) and the critical curve (Bureau and Keppler, 1999) are experimentally determined. Numbers refer to weight percent of H$_2$O in the liquid phase. b) The positions of wet solidi based on experiments in different systems: granite (Huang and Wyllie, 1981; Holtz et al., 2001), pelite solid line (Nichols et al., 1994) and dashed line (Schmidt et al., 2004), basalt (Lambert and Wyllie, 1972) and dashed line according to Kessel et al. (2005a) and peridotite (Green, 1973). Note that up to about 30–35 kbar, the positions of the wet solidi is well constrained by these experiments. Above these pressures there exists considerable uncertainties and further experiments are needed to define more exactly the positions of the solidi and their second critical endpoints. See text for discussion.

little information. Stalder et al. (2001) suggested that in the simplified system MgO–SiO$_2$–H$_2$O the second critical point is at about 120 kbar, 1150 °C. It is expected that in a lherzolite composition the second critical endpoint is at lower pressure. Fig. 2b displays a summary of wet solidi for some key end-member systems with estimated positions of the second critical endpoint. Up to ∼30 kbar the systems are well defined by experiments. At higher pressures, there are still considerable uncertainties. Clearly more experimental work is needed to define the position of the wet solidi and especially the locations of the second critical endpoints.

3.2. Source of fluids

Generally, the source of fluid in HP and UHP rocks derives from dehydration reactions of hydrous phases. There have been extensive reviews about this argument in recent times (Schmidt and Poli, 1998; Poli and Schmidt, 2002; Hacker et al., 2003) and thus we only briefly summarise some key features (Fig. 3). There are

a great variety of hydrous phases in basaltic rocks that generally form a wide range of solid solutions. Hence, most dehydration reactions are continuous and consequently there is a gradual fluid release during prograde subduction, which is dependent on the bulk rock composition (Schmidt and Poli, 1998). At a wide range of UHP conditions, mafic rocks consist of nominally anhydrous minerals. Ultramafic rocks display a much smaller variation in bulk rock composition and solid solutions in key minerals are much more limited than in mafic rocks. As a consequence, ultramafic rocks tend to undergo episodic dehydration. The most important dehydration reaction is the breakdown of antigorite that can release up to 12 wt.% of H$_2$O (Ulmer and Trommsdorff, 1995). Similarly to mafic rocks, ultramafic rocks also consist of nominally anhydrous minerals at most UHP conditions. It is expected that pelitic rocks behave in a similar way to mafic rocks during prograde subduction with continuous reactions consuming hydrous phases. However, the large stability field of phengite prevents complete dehydration of pelites (Hermann, 2002b; Schmidt et al., 2004) and K-bearing
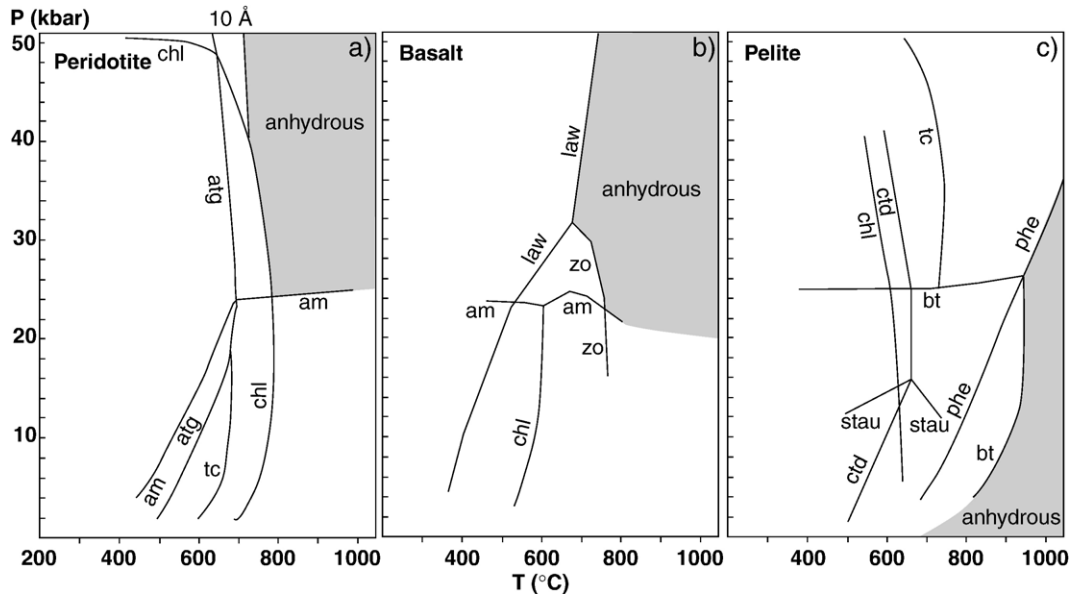
Fig. 3. The stability of hydrous phases in different chemical systems modified from data given by Poli and Schmidt (2002), Hermann (2002b) and Schmidt et al. (2004). The breakdown of hydrous phases in basaltic and pelitic systems will be gradual and dependant on bulk rock composition. Hence the given phase stability limits are an approximation. See text for discussion. Abbreviations: atg=antigorite, tc=talc, am=amphibole; chl=chlorite, 10 Å=10 Å-phase, law=lawsonite, zo=zoisite, phe=phengite; bt=biotite; stau=staurolite; ctd=chloritoide.

mafic rocks (Schmidt and Poli, 1998; Patiño Douce, 2005) and thus they are still hydrous for most UHP conditions.

3.3. Fluid composition

It is relatively easy to characterise hydrous melts as they quench to a glass, which can be analysed by electron microprobe, laser-ablation ICP–MS, infra red spectroscopy and other methods. Results of such studies show that hydrous rhyolitic melts are produced in pelites and granites (Huang and Wyllie, 1981; Nichols et al., 1994; Patiño Douce and Mc Carthy, 1998; Hermann and Green, 2001), dacitic melts are produced in mafic rocks (Lambert and Wyllie, 1972; Yaxley and Green, 1998) and basaltic melts are produced in peridotites (Green et al., 1987). Generally, the water content of the melt increases with increasing pressure and decreasing temperature at UHP conditions (Hermann, 2003). While the phase assemblages in mafic to felsic rocks are very different at low pressures, at UHP conditions they converge to a common assemblage (with different proportions) of coesite, garnet, clinopyroxene, phengite, and kyanite as major minerals and rutile, zircon, apatite and allanite as accessory minerals (Hermann and Green, 2001; Hermann, 2002a; Schmidt et al., 2004). In such a mineral assemblage, the composition of a coexisting melt will be characterised by very low HREE abun-

dances because garnet is present in the residue. LILE are controlled by phengite, LREE, Th and partly U by allanite, Ti, Nb and Ta by rutile, Zr, Hf and partly U by zircon and P by apatite for most cases (Sorensen, 1991; Tribuzio et al., 1996; Zack et al., 2001; Hermann, 2002a; Rubatto and Hermann, 2003). Sr and Pb, two elements that are often used for isotope studies, are controlled by a wide range of minerals including clinopyroxene, phengite, allanite and apatite (Hermann, 2002a; Spandler et al., 2003).

Compared to glasses, it is much more difficult to characterise aqueous fluids as they cannot be quenched. In general, whatever approach is used to constrain the fluid composition of a system, it has to be considered that the fluid composition may be a function of: 1) bulk composition; 2) temperature and pressure; 3) phases which buffer the fluid composition; and, 4) fluid–rock ratio. The most rigorous method for major element solubilities are experiments where the weight loss of a single crystal is determined in H_2O or well known solutions. This has been successfully done for quartz (Manning, 1994) as well as for some minor minerals such as rutile (Tropper and Manning, 2005). Such results provide a data set that may be evaluated by thermodynamic means and can potentially be used to characterise more complex systems (Manning, 2004). For example, Manning (1998) suggested that a fluid in equilibrium with eclogite at the blueschist to eclogite

facies transition is quite dilute and contains a total amount of ∼4.8 wt.% solutes, dominated by Si and Na, followed by Al as the most abundant elements. A different approach is to try to buffer the fluid by a residue consisting of key minerals and determine major and trace element composition of such a buffered fluid. Some early work used perforated capsules and attempted to constrain the fluid composition by element loss from the residue (Kogiso et al., 1997). These authors calculated that about 40–80% of LILE, Sr, Pb and LREE and about 30% of Th and U were lost from a K-bearing amphibolite at 55 kbar and 900 °C. It must be noted that these conditions are close to where the fluid is transitional between an aqueous fluid and a hydrous melt in such a bulk system. Also, in such an extraction experiment, there is no proof that the fluid was in equilibrium with the residue. Very good results on aqueous fluid-hydrous melt trace element partitioning was obtained where fluid quench was directly analysed by laser-ablation ICP-MS or by ion probe. Recent dehydration experiments, where the solid material was contained in a separate crimped capsule (Green and Adam, 2003), provided excellent results on fluid compositions and trace element partitioning. These experiments showed that at conditions of 650–700 °C at 30 kbar, significant amounts of LILE and Sr enter the aqueous fluid whereas REE, Th, U and HFSE are nearly completely retained in the residue. Another promising technique to characterise major and trace element compositions of aqueous fluids is the use of diamond traps (Stalder et al., 1998; Johnson and Plank, 1999; Tenthorey and Hermann, 2004; Kessel et al., 2005a). Although elegant, the diamond trap experiments are not always unambiguous. Firstly, laser-ablation ICP-MS of fluids requires an internal standard that is not always easy to obtain. Doping with Cs has proven to be a promising method to overcome this problem (Tenthorey and Hermann, 2004; Kessel et al., 2005a). Secondly, there is not always complete separation from fluid quench material and residue. This can be due to physical introduction of solid material into the diamond trap at high pressures, or to precipitation of phases out of the fluid within the diamond trap. Our own observations indicate that the latter is nearly always present but the amount of such phases can be monitored within the trap by optical and electron microscopy. A consequence of these problems is that fluid/residue partitioning converges to unity. This is evident in the Johnson and Plank (1999) data for aqueous fluid in equilibrium with a pelite residue and hence the use of these data to model trace element transfer subduction zones is limited. Kessel et al. (2005b) obtained a set of fluid-residue partitioning in a K-free basalt–H$_2$O system as a function

of temperature at 40 and 60 kbar, that shows a much wider range of fluid/solid partitioning than the data of Johnson and Plank (1999). The data of Kessel et al. (2005b) indicates that, apart from LILE, all elements are preferentially incorporated in the residue at 700 °C and 40 kbar. With increasing temperature, the fluid/solid partitioning of all elements increases. It must be noted that the data presented in the Kessel et al. (2005b) paper is only valid for a garnet + clinopyroxene + fluid system and hence its application to trace element transfer in subduction zones is somewhat limited. Key elements such as LILE, LREE and HFSE are not buffered by appropriate phases such as phengite, allanite, zircon and rutile. A new technique, that is presently under development, and has provided very promising results, is trapping of synthetic fluid inclusions at HP conditions (Spandler, 2005). A completely different approach to study HP and UHP fluids is by determination of partition coefficients between mineral and fluids/melts and then combine this information with the trace element concentration of natural minerals (see below). Such data has been obtained successfully for different systems using either large fluid filled capsules (Brenan et al., 1995), diamond traps (Stalder et al., 1998) or otherwise separated quench material (Green and Adam, 2003).

4. Constraints from natural rocks

4.1. Evidence from fluid inclusions

Perhaps the greatest insight into the nature and composition of fluids from HP and UHP rocks has been attained from studies of fluid inclusions from eclogite-facies rocks. Recent reviews by Scambelluri and Philippot (2001) and Touret and Frezzotti (2003) provide a comprehensive evaluation and discussion of these studies, so here we only present an overview of the most important aspects of HP/UHP fluid inclusions.

Fluid inclusions have been described from a range of eclogite-facies rocks, including mafic rocks (Philippot and Selverstone, 1991; Selverstone et al., 1992; Nadeau et al., 1993), pelitic rocks (Agard et al., 2000) and ultramafic rocks (Scambelluri et al., 1997, 2001). However, most of these rock suites have only experienced maximum metamorphic temperatures of 700 °C or lower. A great diversity of fluid inclusion types are commonly preserved, moreover, in some cases, variations between individual inclusion compositions exist on the mm scale (Selverstone et al., 1992). Inclusions may be primary or secondary in origin, with primary inclusions often hosted in HP minerals such as garnet or omphacite. The most common inclusion types are low

salinity aqueous inclusions, which are nearly ubiquitous in all examined rock suites. In many cases, brine inclusions of varying salinity have also been described, with the most saline brines often found in veins (Scambelluri and Philippot, 2001). Some inclusions contain in excess of 50 wt.% solutes and daughter minerals including salts, carbonates, Fe–Ti oxides, phosphates, sulfates, and hydrous silicates. N_2 inclusions formed during decomposition of NH_4-bearing mica have been described from the eclogites of Western Norway (Anderson et al., 1991) and Dabie Shan (Fu et al., 2001), but N_2 tends to be a minor component of fluids from most HP/UHP terranes. CO_2 and CH_4 inclusions are relatively rare (Scambelluri and Philippot, 2001; Touret and Frezzotti, 2003).

At first it seems that a vast range of fluid compositions may accompany HP/UHP metamorphism. However, the observed variability in fluid inclusions is rather a function of localised fluid–rock interactions prior to or during trapping. Moreover, modification can occur during subsequent metamorphism and exhumation. Invariably, the measured density of fluid inclusions is not equivalent to that expected at peak metamorphism, even for primary inclusions in peak metamorphic minerals, as fluid inclusions undergo decrepitation or re-equilibration with the changing $P–T$ conditions accompanying exhumation. Decrepitation may lead to fluid inclusion leakage and modification of the original fluid composition. Highly saline and solute-rich fluid inclusions are also not likely to represent original fluid compositions, as they are likely residues of aqueous fluid–rock interactions or vein formation, where H_2O preferentially partitions into hydrous minerals (Svensen et al., 1999; Scambelluri and Philippot, 2001) or a coexisting melt phase (Philippot, 1993).

There are few studies that include chemical analysis of eclogite-facies fluid inclusions. Scambelluri et al. (2001) present trace element data determined by laser-ablation ICP-MS for fluid inclusions produced by antigorite dehydration in HP ultramafic rocks. As no internal standardisation could be applied to these data, absolute concentrations of the trace elements could not be determined. Nonetheless, the inclusions are clearly enriched in Pb, Sr, and other LILE relative to REE. Similarly, laser-ablation ICP MS analysis of fluid inclusion-rich omphacite domains from an eclogite-facies vein from Monviso (Fig. 4) are enriched in LILE, Pb, Th, and U compared with inclusion-free omphacite domains (Fig. 4). These data indicate the fluid is enriched in LILE, Pb, Th, and U compared to other trace elements. Again, absolute element concentrations in the fluid cannot be calculated, but the results are consistent
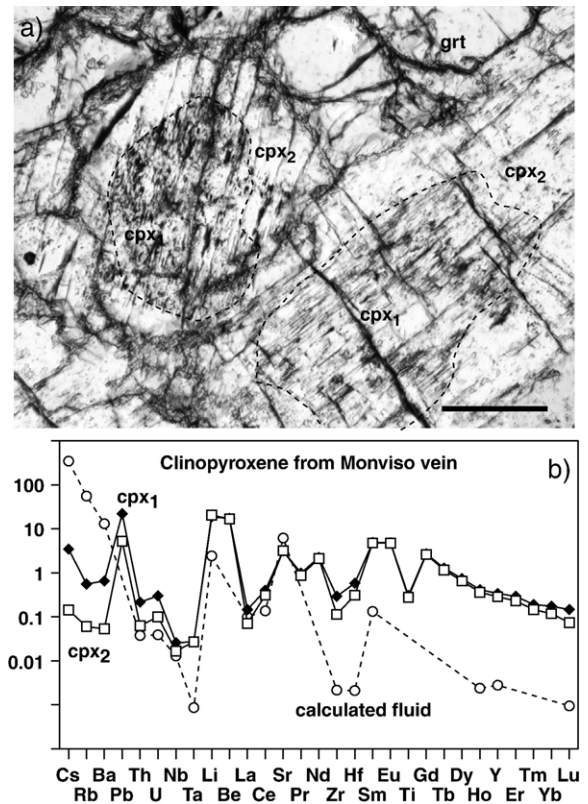

Fig. 4. a) Thin section of a omphacite–garnet–talc–rutile–zircon vein from the Monviso eclogites, Western Alps (Rubatto and Hermann, 2003). Omphacite contains a core with abundant decrepitated fluid inclusions (cpx1), rimmed by clear, inclusion-free omphacite (cpx2). Scale bar represents 200 μm. b) Primitive mantle normalised (McDonough and Sun, 1995) trace element patterns for the omphacite core and rim. A fluid composition in equilibrium with the clear omphacite rims (cpx2) is calculated based on the partitioning given by Green and Adam (2003).

with expected HP fluid compositions as determined experimentally by Green and Adam (2003).

Despite the aforementioned complexities, there is some fundamental information that can be gained from fluid inclusions studies in HP/UHP rocks: Firstly, fluids within low-T (>700 °C) eclogite-facies rocks are dominantly aqueous in composition, which serves as direct evidence for H_2O-rich fluid production by hydrous mineral breakdown during progressive metamorphism. Secondly, the observed small scale variations in fluid compositions in many eclogite terranes, coupled with varying stable isotope signatures (Selverstone et al., 1992), indicates that, in general, fluid flow is highly restricted in well preserved eclogite-facies rocks. Inclusions that contain high solutes contents provide insight into the relative solubility of elements in HP fluids, but have almost certainly undergone passive solute enrichment through water loss and therefore are unlikely to be directly representative of pristine HP aqueous fluids.

4.2. Evidence from high pressure veins

Veins that cut HP/UHP rocks clearly involve fluid in their formation and therefore have the potential to provide critical information on fluid compositions and fluid–rock interaction. Eclogite-facies veins of varying composition have been described from a number of terranes and have previously been interpreted to represent: 1) metamorphosed veins originally formed on the seafloor prior to metamorphism (Widmer et al., 2000); 2) direct and complete precipitates of eclogite-facies fluids (Becker et al., 1999; Gao and Klemd, 2001); 3) products of hydrous mineral breakdown (Castelli et al., 1998); 4) precipitates formed by small scale, closed-system fluid circulation or diffusion (Nadeau et al., 1993; Philippot, 1993; Widmer and Thompson, 2001; Rubatto and Hermann, 2003) or; 5) products of metasomatic interactions between host rock and locally- and externally-derived fluids (Franz et al., 2001; Molina et al., 2004).

Stable isotope and petrologic data indicates that the fluid for most eclogite-facies veins was locally sourced (Nadeau et al., 1993; Becker et al., 1999), and therefore veins do not represent significant fluid channelways (Scambelluri and Philippot, 2001). Instead, many veins are regarded to be products of prolonged small-scale fluid circulation within the host rock (Philippot, 1993), allowing vein growth under high fluid–rock ratio conditions. These conditions lead to precipitation of minerals normally considered to be fluid 'immobile' within the veins. For example, zircon-rich veins from Monviso, Western Alps (Rubatto and Hermann, 2003), garnet-rich veins from New Caledonia (Spandler, 2005) and rutile-bearing veins from Dabie Shan (Franz et al., 2001) and the Tauern Window, Austria (Selverstone et al., 1992) have been described. Similar processes may also explain the LREE-enriched zoisite/clinozoisite segregation preserved in eclogites from the Tauern Window (Brunsmann et al., 2001). In this regard, the veins represent fluid 'cumulates' (Rubatto and Hermann, 2003) or incomplete precipitates of fluids. Therefore determining the composition of fluids from veins directly is a difficult undertaking. We stress that evaluating fluid compositions by directly comparing the geochemistry of bulk veins (or metasomatic selvages to veins) to their host rocks (Becker et al., 1999; Brunsmann et al., 2001; Gao and Klemd, 2001) is unlikely to produce meaningful fluid compositions. However, if the minerals in the vein are regarded to be cumulates, it is possible to calculate a coexisting fluid using appropriate mineral/fluid partitioning. This is shown in Fig. 4 for omphacite from a Monviso vein described in detail by Rubatto and Hermann (2003). Using the omphacite/fluid partitioning of Green and Adam (2003) for basaltic bulk composition determined at 650 °C and 30 kbar and the trace element composition of clean omphacite from the vein, the composition of a coexisting fluid can be calculated. Such a fluid is characterised by elevated contents of Cs (7 ppm), Rb ($\sim$ 30 ppm), Ba ($\sim$ 90 ppm) and Sr ($\sim$ 120 ppm) and probably Pb (no adequate partitioning available) but the concentration of most elements including all REE are well below 1 ppm.

In summary, eclogite-facies veins provide important information of the behaviour of fluids in HP/UHP rocks, but probably relatively little direct information on the geochemical composition of the fluids. Nonetheless, vein minerals may be useful to constrain fluid composition, if appropriate partition coefficients for mineral–fluid are available. In general, the veins indicate that fluid flow is highly restricted in these rocks, which implies that fluid produced during metamorphic devolatilisation may be trapped within the rocks for a significant time period before being released.

4.3. Evidence from changes in bulk rock composition

Progressive dehydration and fluid release accompanies metamorphism up to eclogite facies, meaning that indirect evaluation of relative element solubilities in HP fluids may be gained through analysis of bulk-rock geochemical changes of HP/UHP rocks with metamorphism. Becker et al. (2000) and Arculus et al. (1999) compared mafic eclogites to average MORB and concluded that a large fraction of LILE, and U are lost from eclogite to the fluid during prograde metamorphism. However, oceanic basalts may have highly variable trace element compositions (Spandler et al., 2004) and without accurate comparisons with relevant protoliths these results are somewhat dubious.

Bebout et al. (1999) examined the chemical changes associated with metamorphism of a suite of metasedimentary rocks (greywackes and shales) of varying metamorphic grade from the Catalina Schist. In this case, clear trends of depletion in B, Cs, As, and Sb were observed during the transition from lawsonite–albite blueschist up to amphibolite facies. These rocks were metamorphosed under relatively high temperature conditions and Bebout et al. (1999) stress that element loss is likely to be limited under conditions of HP metamorphism at lower temperatures (<600 °C). This premise is supported by recent studies by Busigny et al. (2003), Chalot Prat et al. (2003) and Spandler et al. (2003, 2004) who compared HP and UHP mafic, ultramafic and metasedimentary rocks to lower-grade or unmetamorphosed equivalent rocks. These studies show that

devolatilisation associated with eclogite-facies metamorphism does not result in significant chemical alteration of the rock, which implies that the fluids released during metamorphism contained low solute contents. By contrast, Breeding et al. (2004) and John et al. (2004) document significant removal of trace elements from HP rocks in zones of channelled fluid flow. Breeding et al. (2004) report in excess of 90% removal of LILE, and Pb from a HP metapelite layer adjacent to a fluid conduit. In these cases element removal was most probably achieved through prolonged low-level dissolution at high fluid–rock ratio conditions, rather than through high element solubilities in the fluid.

4.4. Hydrous melts in UHP gneisses

There is increasing evidence that hydrous granitic melts were present at diamond-facies metamorphism in quartzo-feldspathic rocks. In the Kokchetav Massif, it has been suggested from variation in bulk rock data that garnet- and kyanite-rich gneisses are refractory rocks formed by significant melt extraction (Shatsky et al., 1999). This has been supported by a detailed study on zircon, suggesting that most of the zircon grains formed in the presence of a hydrous granitic melt (Hermann et al., 2001). The most compelling evidence for the presence of hydrous granitic melts stems from polyphase inclusions in garnet found in the Erzgebirge, Germany (Hwang et al., 2001; Stöckhert et al., 2001). These inclusions consist of phlogopite, paragonite, phengite and quartz with minor apatite, rutile and micro-diamond, and are surrounded by radial cracks in the host garnet. These features suggest that the inclusions likely represent trapped hydrous melt at UHP conditions that crystallised and partly reacted with host garnet during cooling and exhumation to form the hydrous minerals. Polyphase silicate inclusions are also
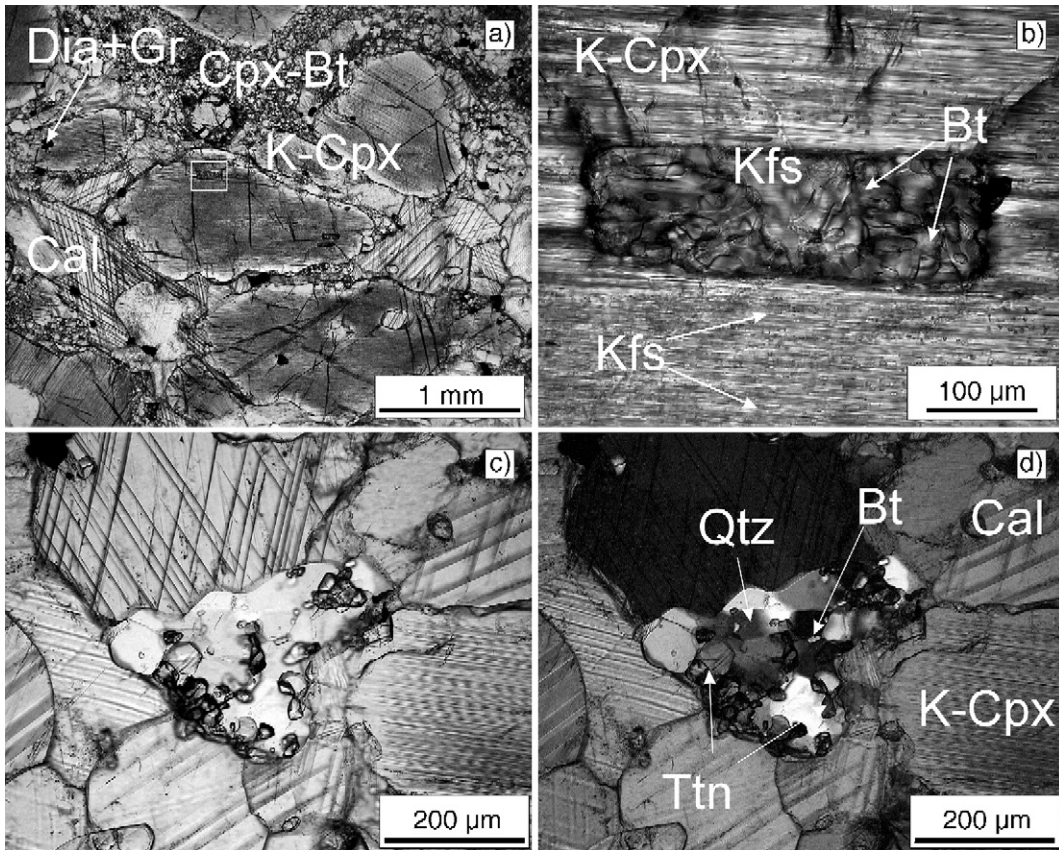

Fig. 5. a) Crystallisation products of UHP hydrous granitic melts in diamond-bearing calcite (Cal) marble (sample G0). Transmitted light (a) and crossed polar (b) microphotograph of Biotite (Bt)+K-feldspar (Kfs) symplectite-like intergrowth as inclusions in a porphyroblast of K_2O-bearing clinopyroxene (K-cpx). Note the negative crystal shape and undisturbed lamellae of Kfs around inclusion, indicating that it was trapped at UHP conditions. Transmitted light (c) and crossed polar (d) microphotograph of a silicate-bearing pocket containing quartz (Qtz), biotite (Bt) and titanite (Ttn) in a carbonate matrix (Cal=Calcite). Inclusions with similar compositions occur in K_2O-bearing clinopyroxene and garnet and have trace element composition typical of rhyolitic melts (Korsakov and Hermann, 2006).

found in the Kokchetav Massif, but mainly in interlayered carbonate rocks rather than in metapelites (Korsakov and Hermann, 2006). The polyphase inclusions occur within garnet and K-bearing clinopyroxene and occasionally form negative crystal shapes (Fig. 5a,b). Often radial cracks starting from the inclusions are found. Two different types of inclusions have been found. The first type mainly consists of a symplectite-like biotite K-feldspar intergrowth with a nearly constant ratio of 1:2. A second type of polyphase silicate inclusions contains significant amounts of titanite and zoisite together with K-feldspar and biotite. Laser Ablation ICP-MS analyses of the second type of inclusions provides evidence that the trace element pattern of the bulk inclusion is very similar to patterns of felsic melts (Korsakov and Hermann, 2006). A tight intergrowth of biotite and K-feldspar is rarely found in the matrix of some carbonates (Figs. 5b,c) suggesting the presence of an intergranular hydrous granitic melt (Korsakov et al., 2004). In a recent comparison between features of quartz-rich diamondiferous rocks in the Kokchetav Massif and in the Erzgebirge, Massonne (2003) concluded that both rock types were most likely partially molten at UHP conditions. In summary, the highest-grade rocks, that are accessible for detailed studies, provide strong evidence that hydrous rhyolithic–dacitic melts may form in deeply subducted felsic rocks.

4.5. Partial melting during decompression

Extensive partial melting in UHP gneissic rocks is probably less common at peak UHP conditions than during exhumation. The main reason for this is related to the stability field of phengite, which is the principal hydrous phase in UHP felsic rocks (Fig. 2). If peak conditions are at relatively low temperatures and cooling occurs during exhumation, as in the case of the Dora Maira Massif (Fig. 6), phengite is stable during the whole prograde and retrograde evolution and the UHP assemblages are well preserved (Chopin et al., 1991; Hermann, 2003). In contrast, if peak metamorphic conditions are greater than 750 °C and decompression is nearly isothermal, fluid-absent melting of phengite occurs during the exhumation of the UHP rocks (Hermann, 2002b). This is well documented in examples like the Sulu UHP belt in China (Nakamura and Hirajima, 2000) and the Ulten zone in the Italian Alps (Tumiati et al., 2003), where UHP metamorphism is followed by granulite facies overprint. Typically the felsic rocks are transformed to migmatites and there is new growth of biotite (Fig. 6). The diamond-bearing gneisses of the Kokchetav Massif were metamorphosed at even higher temperatures and most of the exhumation took place in the presence of partial melts. It has been suggested that such
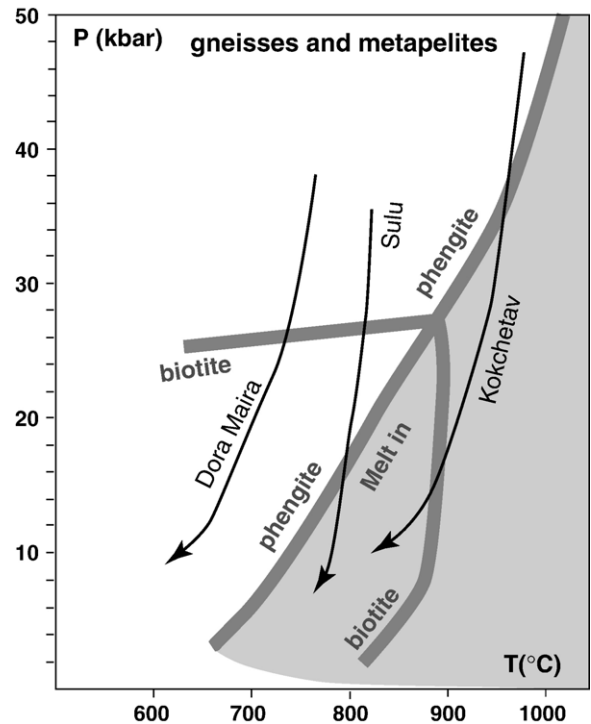

Fig. 6. Partial melting of UHP felsic rocks might occur during exhumation. Phase stability fields are from Hermann (2002b). Exhumation path are shown for Dora-Maira rocks (Compagnoni et al., 1995; Hermann, 2003), Sulu (Nakamura and Hirajima, 2000) and Kokchetav Massif (Shatsky et al., 1995; Hermann et al., 2001).

presence of melts might help in the fast exhumation of such UHP rocks (Hermann and Green, 2001). A major consequence of this fluid-absent melting of phengite is that most information about UHP metamorphism in the felsic rocks will be erased during exhumation apart from inclusions in refractory phases such as garnet, kyanite or zircon (Katayama et al., 2000; Hermann et al., 2001).

4.6. Different types of melts

The majority of research on HP and UHP fluids has been focused on hydrous silicate systems. However, there is increasing evidence that different types of melts might be present at UHP metamorphic conditions, especially in diamond-facies rocks. In the Kokchetav Massif, it has been postulated that polyphase carbonate inclusions found in garnet and clinopyroxene in diamond-bearing marbles might originate from hydrous carbonate melts (Korsakov and Hermann, 2006). Fig. 7a displays such a polyphase inclusion in a dolomite marble. Similar to the silicate polyphase inclusions described above, the carbonate inclusion displays a negative crystal shape and is surrounded by radial fractures in the garnet host (Fig.

7c). The inclusion consists of Mg-calcite showing dolomite exsolution lamellae, whereas the matrix carbonate is pure dolomite. Fig. 7d shows that the trace element composition of the Mg-calcite inclusion is different from the matrix dolomite. Furthermore, the composition is also different from the trace element composition of an inferred Mg-calcite that would be in equilibrium with dolomite, using an empirical Mg-calcite/dolomite trace element partitioning from rocks where both types of carbonates co-exist (Korsakov and Hermann, 2006). The Mg-calcite inclusion has higher LREE and lower HREE than expected for a solid Mg-calcite in equilibrium with dolomite. The inclusion also displays a positive Ba anomaly with respect to Rb and Cs and U>Th, features that are common in UHP fluid phases (Malaspina et al., 2005). Occasionally, inclusions display a corona of small rounded carbonate droplets, a texture that is interpreted to document an initial stage of

decrepitation (Korsakov and Hermann, 2006). In summary, four key observations are found in such inclusions: 1) negative crystal shape; 2) radial cracks; 3) textures indicative of decrepitation; and, 4) different major and trace element composition than matrix carbonates. These observations indicate that hydrous (?) carbonate melts were possibly present at UHP metamorphic conditions.

In the same rocks sulfides (approximate composition: FeS) also form peculiar textures. They occur in clusters, contain small crystals of silicates and are surrounded by radial cracks and tiny sulfide droplets (Fig. 7a). The radial cracks are often decorated by irregular shaped sulfides, which display similar textural features as cracks healed in the presence of fluids. Such features have been interpreted to represent decrepitated sulfide melt inclusions (Frost et al., 2002). Therefore it seems possible that sulfide melts could also be present at UHP conditions. We suggest that the inclusions represent
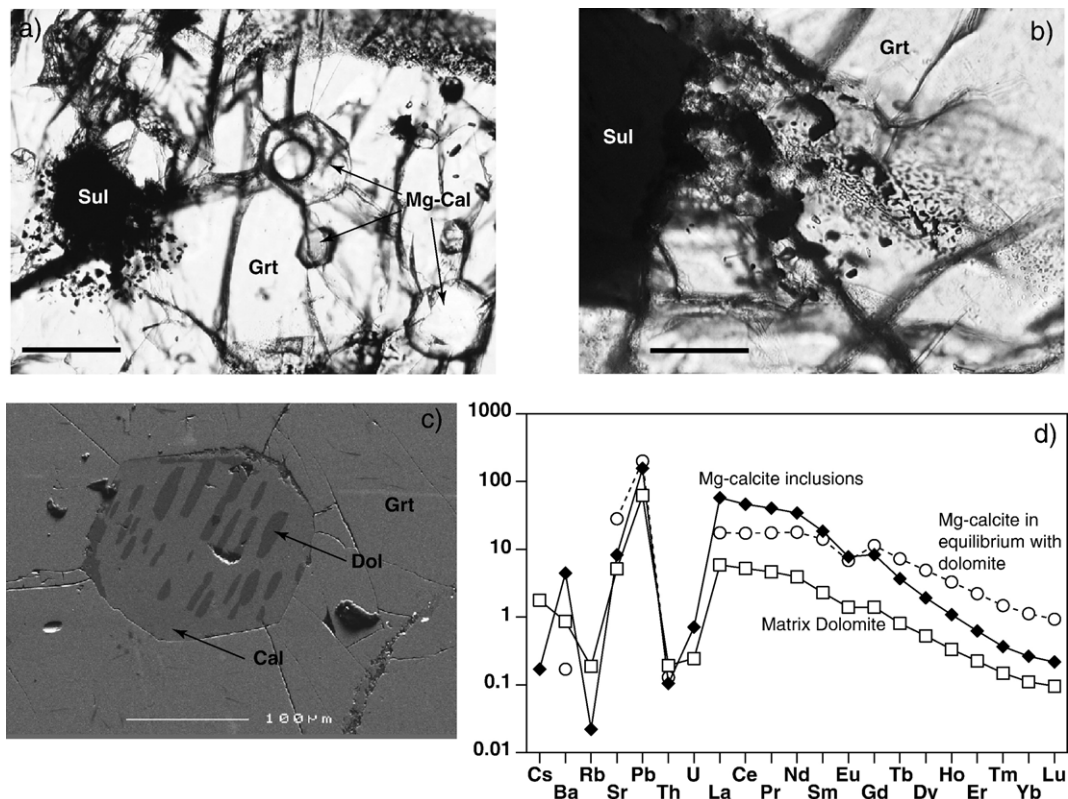

Fig. 7. a) Photomicrograph of garnet (Grt) from a dolomite marble (EK 21), Kokchetav Massif, containing Mg-calcite (Mg-Cal) and sulfide (Sul) inclusions. Note that the Mg-calcite inclusions display negative crystal shapes of the host garnet (a). Round pit represents site of laser ablation analysis. The sulfide inclusion is surrounded by small sulfide droplets. Scale bar represents 200 μm. b) A radial fracture departing from a sulfide inclusion is decorated with tiny sulfide droplets, suggesting that a sulfide liquid was present at UHP conditions. Scale bar is 100 μm. c) BSE image of inclusion analysed by LA-ICP-MS. The inclusion displays a negative crystal shape and is surrounded by radial cracks. The initial Mg-calcite inclusion exsolved into calcite (Cal) and dolomite (Dol) during the retrograde evolution. d) Primitive mantle normalised (McDonough and Sun, 1995) trace element patterns for matrix dolomite and Mg-calcite inclusion. Also shown is the pattern of solid Mg-calcite that would be in equilibrium with dolomite. See text for discussion.

residual sulfides that have lost some low melt fraction elements during decrepitation. Polyphase Ni–Fe–S inclusions in garnet have been described from garnetite layers within UHP garnet peridotites from the Sulu terrane (Zhang et al., 2004). Based on the texture and composition, the authors suggested that these inclusions derive from a trapped Ni-rich sulfide melt. However, it is not clear whether such a sulfide melt formed in a mantle environment prior to subduction or whether it was present at UHP conditions. More work is needed to consolidate the hypothesis of different types of melts at diamond-facies conditions.

5. Discussion and conclusions

5.1. Nature of the fluid phase

The recognition that in felsic systems there is a second critical endpoint terminating the wet solidus at conditions that can be encountered by UHP rocks (Fig. 2) led to considerable confusion regarding the terminology for UHP-fluids. Often the term "supercritical fluid" is used, whereas this is valid for the whole region where one fluid phase exists. For example, a single fluid phase can exist at amphibolite facies conditions (Fig. 1), and hence the term "supercritical fluid" is not useful at all. We suggest that the fluid phase present at HP and UHP conditions should be characterised by its composition and physical properties. In HP and UHP rocks a fluid will always co-exist with a solid residue and hence the amounts of solutes in the fluid will be buffered by the rock. We use the term aqueous fluid for a water-rich fluid phase that contains less than ∼30 wt.% of solutes, whereas a fluid phase with ∼65 wt.% or more solutes has the properties of a hydrous melt. In between there is a transitional region that typically extends for about a 100 °C interval where the total amount of solutes strongly increases with increasing temperature (Fig. 1). The position of this transitional region is determined by the termination of the wet solidus and the second critical endpoint.

Fig. 8a shows how the nature of a fluid phase can be approximated in pelitic rocks that underwent different
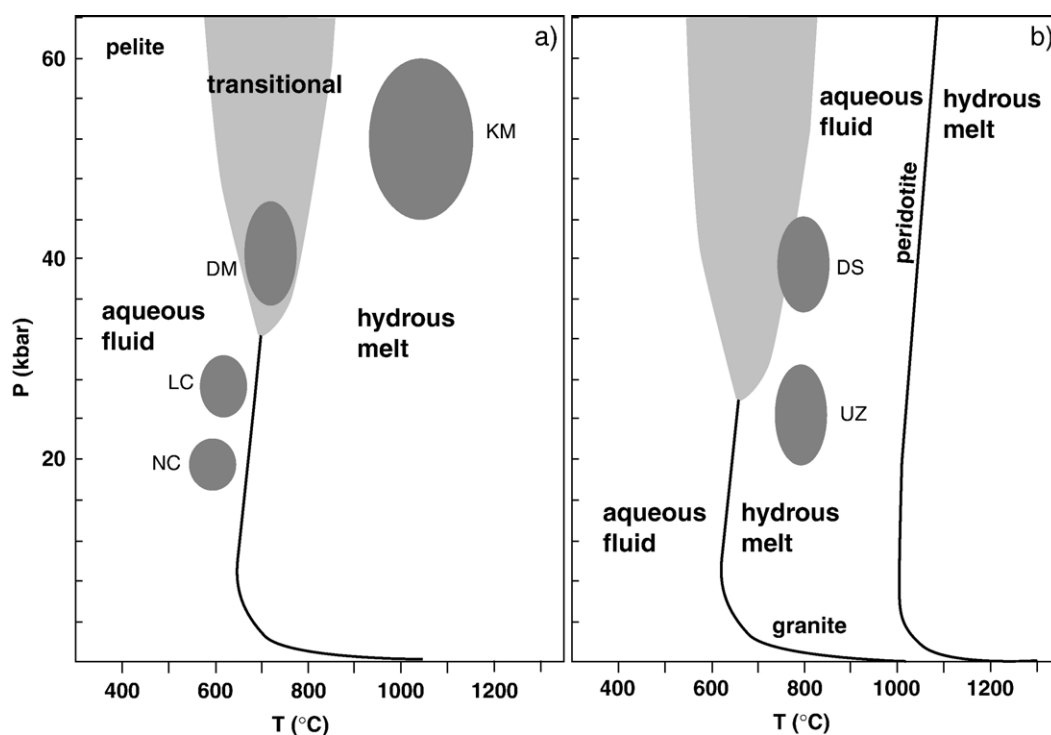

Fig. 8. The position of peak metamorphic conditions with respect to the wet solidus provides a first order information on the nature of the fluid phase present. a) Aqueous fluid must be present at eclogite facies metamorphism in the New Caledonia (NC) and the Lago di Cignana (LC) metapelites, whereas the felsic rocks from the Kokchetav Massif are situated well within the field of hydrous melts. The pelitic rocks of the Dora Maira Massif (DM) plot in the field where the fluid phase is likely to be transitional between a hydrous felsic melt and an aqueous fluid. b) Bulk rock composition strongly constrains the nature of the fluid phase. At peak metamorphic conditions in the Central Dabie Shan (DS) and Ulten Zone (UZ) rocks, a hydrous granitic melt is likely to be present in the country rock gneisses whereas in ultramafic lenses, an aqueous fluid is stable. Such rock suites are important natural laboratories for element transfer in subduction zones as they show in which ways hydrous granitic melts produced in subducted sediments will react with the overlaying mantle wedge.

peak metamorphic conditions. Metasediments in the New-Caledonia HP terrain reached peak conditions of ~ 600 °C and ~ 20 kbar (Spandler et al., 2003). This $P–T$ region is clearly at lower temperatures than the wet solidus and at pressures lower than the second critical endpoint. Hence an aqueous fluid must have been present at peak conditions. Higher pressures of up to 27 kbar have been documented in the metasediments of Lago di Cignana (Western Alps) where coesite has been found (Reinecke, 1998). Although it is expected that the amount of solutes in the fluid will be significantly larger than in New Caledonia, it still plots in the field where an aqueous fluid is stable. On the other hand, diamondiferous pelitic rocks such as the ones found in the Kokchetav Massif experienced peak metamorphic conditions that are well within the stability field of hydrous melts (Shatsky et al., 1995; Hermann et al., 2001). As we pointed out above, this is in agreement with increasing geological evidence for the presence of hydrous silicate melts in these rocks. Because the second critical endpoint in pelitic systems is likely to be at ~ 30 kbar, there is the potential that some UHP terrains will be situated in the region, where fluids are transitional. In fact, the $P–T$ estimates for the Dora-Maira Massif (Western Alps) are exactly in this region (Fig. 8a; Chopin et al., 1991; Compagnoni et al., 1995; Hermann, 2003). Recently, primary polyphase inclusions with similar characteristics to the polyphyse inclusion from the Kokchetav Massif have been found in peak metamorphic minerals in quartzites and eclogites from the Sulu UHP region (Ferrando et al., 2005). The authors argued that these polyphase inclusions represent precipitates from a fluid with transitional character between aqueous fluid and hydrous melt. The peak $P–T$ conditions for the samples were estimated at 840 ± 50 °C, 35–40 kbar and are likely situated in the field of hydrous melts for the investigated rock systems, close to the transitional zone, in good agreement with the interpretation of the authors that the inclusions derive from solute-rich liquids. The hypothesis that some polyphase inclusions derive from trapped melt has been supported by experiments of Perchuk et al. (2005), who demonstrated that polyphase inclusions within garnet could be rehomogenised to hydrous silicate melts at UHP conditions. Although polyphase inclusions are difficult to interpret due to their reaction with the host minerals during the retrograde evolution, these examples demonstrate that polyphase silicate inclusions will play a crucial role in deciphering the nature and composition of hydrous melts and transitional fluids in UHP rocks.

In most UHP terrains different rock types occur, and thus the fluid composition must change over short dis-

tances. For example in the Ulten zone and in the Dabie Shan, lenses of ultramafic rocks are embedded in gneisses. Geochemical studies have shown that the ultramafic rocks in both places experienced metasomatism close to the peak metamorphic conditions by a fluid phase that has been sourced from crustal rocks (Rampone and Morten, 2001; Jahn et al., 2003). The effect of bulk composition on the properties of the fluid phase in such rock suites is illustrated in Fig. 8b. The general phase relations indicate that a hydrous granitic melt must have been present in the gneisses. In contrast, for the ultramafic rocks, the $P–T$ conditions are still well within the field where an aqueous fluid is stable. This implies that a significant amount of the solutes in the hydrous granitic melt must react with the peridotite in order to produce an aqueous fluid (e.g. Manning, 2004). As the most abundant elements in a hydrous granitic melt are SiO_2 and Al_2O_3, it is expected that orthopyroxene and garnet should form at the interaction zone. Such UHP metasomatic rocks have been recently discovered in the Dabie Shan (Malaspina et al., 2005).

5.2. Implications for phase diagram calculations

The presented phase diagrams (Figs. 1 and 2) show that aqueous fluids and hydrous melts in HP and UHP rocks are much more complex than what is found during normal crustal metamorphism. This has profound implications on the thermodynamic modelling of such rocks. In most models of this nature, the activity of H_2O is set to unity, an assumption is not valid in UHP rocks. For example, Kerrick and Connolly (2001) calculated phase diagrams for deeply subducted sediments. However they did not include the wet solidus of these systems and considered the fluid phase to be an ideal $CO_2–H_2O$ mixture, neglecting any dissolved silicates. Our approach shows that such an assumption might be sustainable for prograde subduction up to about ~ 25 kbar and ~ 650 °C (i.e. in the part where the total amount of solutes in the aqueous fluid are expected to be low). However, at higher metamorphic conditions such as those encountered in UHP terrains or in the subducted slab at sub-arc depth the activity of H_2O will be significantly different from unity and changes as a function of bulk rock composition, P and T.

For the Dora Maira whiteschists, it has been postulated that the activity of H_2O in the fluid must be significantly reduced at peak metamorphic conditions (Sharp et al., 1993, Philippot et al., 1995). Sharp et al. (1993) showed with isotope thermometry that peak temperatures were 700–750 °C. In order to obtain the observed formation of garnet and coesite at the expense of talc and kyanite, they suggested that the activity of

H₂O in the fluid must have been reduced to values of 0.4–0.75. This is in good agreement with the position of the Dora Maira rocks in the transitional region between aqueous fluids and hydrous melts (Fig. 8a). Hence we suggest that dissolved total solids (rather then CO_2 or NaCl) will cause the reduction of the H_2O activity. This has been supported by experiments in the KCMASH system where the formation of garnet and coesite from talc and kyanite was constrained to temperatures of ∼ 730 °C (Hermann, 2003), an experimental observation that is in good agreement with the thermometry. In contrast to thermodynamic calculations, in experimentally determined grids the activity of water has the appropriate value (although not measured) at any pressure and temperature because the fluids are always buffered with an appropriate solid residue.

5.3. Composition of eclogite facies aqueous fluids

The presented data from theoretical phase relations, natural rocks and experiments help to constrain the fluid composition in eclogites that derive from the transition of lawsonite-blueschist to epidote-eclogite. This transition occurs at about 15–25 kbar and 500–600 °C and represents a major dehydration event in subducted crust (Poli and Schmidt, 1995; Hacker et al., 2003). Daughter crystals found in fluid inclusions trapped in eclogite facies minerals indicate that there is considerable solubility of elements in such fluids, but generally the inclusions are dominantly aqueous in composition, in agreement with the phase relations (Fig. 1). Quantification of such fluids indicates that they are surprisingly dilute. Modelling of solubility data showed that they contain less than 5 wt.% total solutes (Manning, 1998) and it is likely that such fluids have only 2–3 times more dissolved total solids than seawater (Manning, 2004). This is in agreement with recent studies on variations in bulk rock compositions across the blueschist to eclogite transition (see above) indicating that even fluid mobile elements are not significantly depleted. Also, very low trace element contents of fluids especially LREE are calculated using the composition of minerals precipitated from fluids and low temperature mineral/fluid partition coefficients (Fig. 4b). All the combined evidence now provides a convincing picture that there is a decoupling of water and trace element release in subducted oceanic crust. While the blueschist to eclogite facies transition is important for liberating an aqueous fluid, it seems that these fluids contain only moderate amounts of LILE, Sr and Pb and do not transport significant amounts of key trace elements such as LREE, U and Th from the slab to the mantle wedge (Fig. 9). As a consequence we suggest that zones where strong depletion of these trace elements occur (Breeding et al., 2004; John
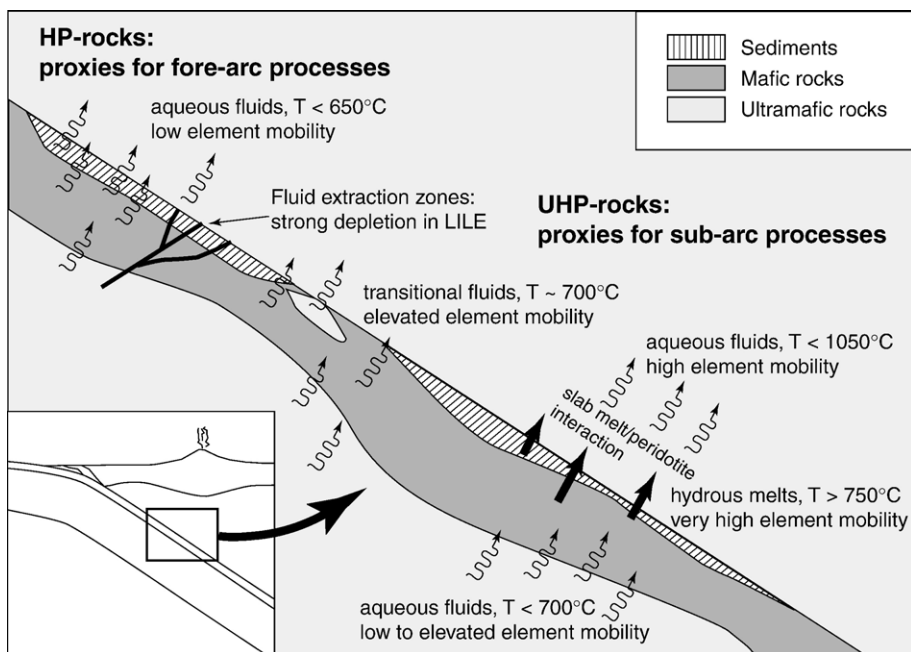

Fig. 9. Schematic occurrence of aqueous fluids and hydrous melts in a subduction zone setting. Natural high-pressure and ultra-high pressure rocks can be used to infer fore-arc and sub-arc processes, respectively. See text for discussion.

et al., 2004) must reflect high fluid–rock ratio and probably represent pathways of aqueous fluid extraction (Fig. 9).

5.4. Element transfer from slab to mantle wedge

It is well known that arc lavas contain a "subduction component" that derives from the subducted crust and is transferred to the locus of partial mantle melting by a fluid phase (Plank and Langmuir, 1993; Elliott, 2003). This subduction component is enriched in LILE, Th and U and varying amounts of LREE. From the considerations above, it is evident that oceanic crust in the fore-arc region at a depth of ~ 70 km and temperatures of ~ 600 °C still contains a large amount of LILE, LREE, U and Th. This implies that these elements are still available for extraction at sub-arc depth. The theoretical phase relations show that with increasing temperature, the amount of solutes in the fluid phase drastically increase independent of whether the rocks pass through the wet solidus or whether they evolve above the second critical endpoint (Fig. 1). Because the wet solidi for granitic, pelitic and mafic rocks are very similar (Fig. 2b), the critical temperature interval where solubilities strongly increase in subducted crust is at 700–750 °C at a sub-arc depths of 100–150 km. Therefore, we suggest that the primary agent leading to mantle metasomatism is a hydrous melt rather than an aqueous fluid. It has been shown by experiments (Kogiso et al., 1997; Rapp et al., 1999; Hermann and Green, 2001) as well as by the studies of UHP rocks from the Kokchetav Massif (Shatsky et al., 1999; Korsakov and Hermann, 2006) that large amounts of the elements enriched in arc lavas can be transported by hydrous granitic melts. How these trace elements are transported to the locus of partial melting in the mantle wedge is still a matter of debate. If the hydrous granitic melts are generated at temperatures below the wet peridotite solidus (Fig. 8), a great amount of solutes will precipitate when the melts contacts the mantle wedge peridotite and the trace elements are likely to be transported by an aqueous fluid within the sub-arc mantle wedge (Fig. 9).

Subducted sediments are the main reservoir of key trace elements such as LILE, Th and U (Plank and Langmuir, 1998; Tenthorey and Hermann, 2004). Moreover there is a correlation between the composition of sediment input and arc magmatism demonstrating that the sediments play a key role for the transfer of elements from the slab to the mantle wedge (Plank and Langmuir, 1993; Elliott, 2003). On the other hand, in terms of the H_2O budget, sediments are insignificant because of the relatively small volume of subducted

sediments. Additionally the large stability of phengite (Fig. 3c) prevents significant fluid-absent melting in sediments at sub arc depth. For this reason, it has been suggested that fluid and trace element sources must be decoupled (Hermann and Green, 2001; Spandler et al., 2004). Aqueous fluids can derive from dehydration of ultramafic rocks and probably to a lesser extent from mafic rocks in colder portions of the slab (Figs. 3 and 9), because of the strong temperature gradient within the slab (van Keken et al., 2002). These aqueous fluids can then induce fluid present melting in the sediments and altered oceanic crust (originally MORB) on top of the slab (Nichols et al., 1994; Hermann and Green, 2001).

Finally, we emphasise that the considerations about major and trace element solubilities in HP and UHP aqueous fluids and hydrous melts have some consequences for the thermal structure of subduction zones. We propose that the sediments at the top of the slab need to be hotter than 700–750 °C at sub-arc depth in order to melt and transport key elements from the slab to the mantle wedge. These conditions are hotter than classical numerical models predict, except for relatively rare cases of slow subduction of young oceanic crust (Peacock, 1996; Kincaid and Sacks, 1997). However, recent numerical (van Keken et al., 2002) and analog (Kincaid and Griffiths, 2004) modelling suggested that the top of the slab might be significantly hotter than previously thought allowing the uppermost section of the slab to melt.

Acknowledgements

References

Agard, C., Goffé, B., Touret, J.L.R., Vidal, O., 2000. Retrograde mineral and fluid evolution in high-pressure metapelites (Schists Lustrés Unit, Western Alps). Contributions to Mineralogy and Petrology 140, 296–315.

Anderson, T., Austrheim, H., Burke, E.A.J., 1991. Mineral–fluid–melt interactions in high-pressure shear zones, Bergen Arcs nappe complex, Caledonides of western Norway: implications for fluid regime in Caledonian eclogite facies metamorphism. Lithos 27, 187–204.

Arculus, R.J., Lapierre, H., Jaillard, E., 1999. Geochemical window into subduction and accretion processes; Raspas metamorphic complex, Ecuador. Geology 27, 547–550.

Austrheim, H., 1987. Eclogitization of lower crustal granulites by fluid migration through shear zones. Earth and Planetary Science Letters 81, 221–232.

Bebout, G.E., Ryan, J.G., Leeman, W.P., Bebout, A.E., 1999. Fractionation of trace elements by subduction-zone metamorphism; effect of

convergent-margin thermal evolution. Earth and Planetary Science Letters 171, 63–81.

Becker, H., Jochum, K.P., Carlson, R.W., 1999. Constraints from high-pressure veins in eclogites on the composition of hydrous fluids in subduction zones. Chemical Geology 160, 291–308.

Becker, H., Jochum, K.P., Carlson, R.W., 2000. Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones. Chemical Geology 163, 65–99.

Boettcher, A.L., Wyllie, P.J., 1969. System CaO–SiO_2–CO_2–H_2O. Second critical end-point on the melting curve. Geochimica et Cosmochimica Acta 33, 611–632.

Breeding, C.M., Ague, J.J., Bröcker, M., 2004. Fluid–metasedimentary rock interactions in subduction-zone mélange: implications for the chemical composition of arc magmas. Geology 31, 1041–1044.

Brenan, J.M., Shaw, F.F., Ryerson, F.J., Phinney, D.L., 1995. Mineral-aqueous fluid partitioning of trace elements at 900 °C and 2.0 GPa: constraints on the trace element chemistry of mantle and deep crustal fluids. Geochimica et Cosmochimica Acta 59, 3331–3350.

Brunsmann, A., Franz, G., Erzinger, J., 2001. REE mobilization during small-scale high-pressure fluid–rock interaction and zoisite/fluid partitioning of La to Eu. Geochimica et Cosmochimica Acta 65, 559–570.

Bureau, H., Keppler, H., 1999. Complete miscibility between silicate melts and hydrous fluids in the upper mantle: experimental evidence and geochemical implications. Earth and Planetary Science Letters 165, 187–196.

Busigny, V., Cartigny, P., Philippot, P., Ader, M., Javoy, M., 2003. Massive recycling of nitrogen and other fluid mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schists Lustrés nappe (Western Alps, Europe). Earth and Planetary Science Letters 215, 27–42.

Castelli, D., Rolfo, F., Compagnoni, R., Xu, S., 1998. Metamorphic veins with kyanite, zoisite and quartz in the Zhu-Jia-Chong eclogite, Dabie Shan, China. The Island Arc 7, 159–173.

Chalot-Prat, F., Ganne, J., Lombard, A., 2003. No significant element transfer from the oceanic plate to the mantle wedge during subduction and exhumation of the Tethys lithosphere (Western Alps). Lithos 69, 69–103.

Chopin, C., Henry, C., Michard, A., 1991. Geology and petrology of the coesite-bearing terrain, Dora Maira Massif, Western Alps. European Journal of Mineralogy 3, 263–291.

Compagnoni, R., Hirajima, T., Chopin, C., 1995. Ultra-high-pressure metamorphic rocks in the Western Alps. In: Coleman, R.G., Wang, X. (Eds.), Ultrahigh Pressure Metamorphism. Cambridge University Press, Cambridge, UK, pp. 206–243.

Elliott, T., 2003. Tracers of the slab. In: Eiler, J. (Ed.), Inside the Subduction Factory. Geophysical Monograph, vol. 138. American Geophysical Union, Washington D.C., pp. 23–45.

Ferrando, S., Frezzotti, M.L., Dallai, L., Compagnoni, R., 2005. Multiphase solid inclusions in UHP rocks (Su-Lu, China): remnants of supercritical silicate-rich aqueous fluids released during continental subduction. Chemical Geology 223, 82–92.

Franz, L., Romer, R.L., Klemd, R., Schmid, R., Oberhänsli, R., Wagner, T., 2001. Eclogite-facies quartz veins within metabasites of the Dabie Shan (eastern China): pressure–temperature–time–deformation path, composition of the fluid phase and fluid flow during exhumation of high-pressure rocks. Contributions to Mineralogy and Petrology 141, 322–346.

Frost, B.R., Mavrogenes, J.A., Tomkins, A.G., 2002. Partial melting of sulfide ore deposits during medium and high grade metamorphism. Canadian Mineralogist 40, 1–18.

Fu, B., Touret, J.L.R., Zheng, Y.F., 2001. Fluid inclusions in coesite-bearing eclogites and jadeite quartzite at Shuanghe, Dabie Shan (China). Journal of Metamorphic Geology 19, 529–545.

Gao, J., Klemd, R., 2001. Primary fluids entrapped at blueschist to eclogite transition: evidence from the Tianshan meta-subduction complex in northwestern China. Contributions to Mineralogy and Petrology 142, 1–14.

Green, D.H., 1973. Experimental melting studies on a model upper mantle composition at high pressure under water-saturated and water-undersaturated conditions. Earth and Planetary Science Letters 19, 37–53.

Green, T.H., Adam, J., 2003. Experimentally-determined trace element characteristics of aqueous fluid from dehydrated mafic oceanic crust at 3.0 GPa, 650–700 °C. European Journal of Mineralogy 15, 815–830.

Green, D.H., Fallon, T.J., Taylor, W.R., 1987. Mantle-derived magmas — roles of variable source peridotite and variable C–H–O fluid compositions. In: Myson, B.O. (Ed.), Magmatic Processes: Physiochemical Principles. The Geochemical Society Special Publication, pp. 139–154.

Hacker, B.R., Abers, G.A., Peacock, S.M., 2003. Subduction factory 1. Theoretical mineralogy, densities, seismic wave speeds, and H_2O contents. Journal of Geophysical Research 108, 2029–2054.

Heinrich, C.A., 1982. Kyanite-eclogite to amphibolite facies evolution of hydrous mafic and pelitic rocks, Adula nappe, Central Alps. Contributions to Mineralogy and Petrology 81, 30–38.

Hermann, J., 2002a. Allanite: thorium and light rare earth element carrier in subducted crust. Chemical Geology 192, 289–306.

Hermann, J., 2002b. Experimental constraints on phase relations in subducted continental crust. Contributions to Mineralogy and Petrology 143, 219–235.

Hermann, J., 2003. Experimental evidence for diamond-facies metamorphism in the Dora-Maira Massif. Lithos 70, 163–182.

Hermann, J., Green, D.H., 2001. Experimental constraints on high pressure melting in subducted crust. Earth and Planetary Science Letters 188, 149–186.

Hermann, J., Rubatto, D., Korsakov, A., Shatsky, V.S., 2001. Multiple zircon growth during fast exhumation of diamondiferous, deeply subducted continental crust (Kokchetav Massif, Kazakhstan). Contributions to Mineralogy and Petrology 141, 66–82.

Holtz, F., Becker, A., Freise, M., Johannes, W., 2001. The water-undersaturated and dry Qz–Ab–Or system revisited. Experimental results at very low water activities and geological implications. Contributions to Mineralogy and Petrology 141, 347–357.

Huang, W.L., Wyllie, P.J., 1981. Phase relationships of S-type granite with H_2O to 35 kbar: muscovite granite from Harney Peak, south Dakota. Journal of Geophysical Research 86, 10515–10529.

Hwang, S.-L., Shen, P., Chu, H.-T., Yui, T.-F., Lin, C.-C., 2001. Genesis of microdiamonds from melt and associated multiphase inclusions in garnet of ultrahigh-pressure gneiss from Erzgebirge, Germany. Earth and Planetary Science Letters 188, 9–15.

Jahn, B.-M., Fan, Q., Yang, J.-J., Henin, O., 2003. Petrogenesis of the Maowu Pyroxenite-Eclogite Body from the UHP Metamorphic Terrane of Dabieshan: Chemical and Isotopic Constraints.

John, T., Scherer, E.E., Haase, K., Schenk, V., 2004. Trace element fractionation during fluid-induced eclogitization in a subducting slab: trace element and Lu–Hf–Sm–Nd isotope systematics. Earth and Planetary Science Letters 227, 441–456.

Johnson, M.C., Plank, T., 1999. Dehydration and melting experiments constrain the fate of subducted sediments. Geochemistry Geophysics Geosystems 1 (1999GC000014).

Katayama, I., Zayachkovsky, A.A., Maruyama, S., 2000. Prograde pressure–temperature records from inclusions in zircons from the

ultrahigh-pressure–high pressure rocks of the Kokchetav Massif, northern Kazakhstan. The Island Arc 9, 417–427.

Kennedy, G.C., Heard, H.C., Wasserburg, G.J., Newton, R.C., 1962. The upper three-phase region in the system SiO_2–H_2O. American Journal of Science 260, 501–521.

Kerrick, D.M., Connolly, J.A.D., 2001. Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. Nature 411, 293–296.

Kessel, R., Ulmer, P., Pettke, T., Schmidt, M.W., Thompson, A.B., 2005a. The water-basalt system at 4 to 6 GPa: phase relations and second critical endpoint in a K-free eclogite at 700 to 1400 °C. Earth and Planetary Science Letters 273, 873–892.

Kessel, R., Schmidt, M.W., Ulmer, P., Pettke, T., 2005b. Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. Nature 437, 724–727.

Kincaid, C., Griffiths, R.W., 2004. Variability in flow and temperature within mantle subduction zones. Geochemistry, Geophysics, Geosystems 5, Q06002.

Kincaid, C., Sacks, I.S., 1997. Thermal and dynamical evolution of the upper mantle in subduction zones. Journal of Geophysical Research 102, 12295–12315.

Kogiso, T., Tatsumi, Y., Nakano, S., 1997. Trace element transport during dehydration processes in the subducted oceanic crust. 1. Experiments and implications of the origin of ocean island basalts. Earth and Planetary Science Letters 148, 193–205.

Korsakov, A.V., Hermann, J., 2006. Silicate and carbonate melt inclusions associated with diamonds in deeply subducted carbonate rocks. Earth and Planetary Science Letters 241, 104–118.

Korsakov, A.V., Theunissen, K., Smirnova, L.V., 2004. Intergranular diamond derived from partial melting of rocks at ultrahigh-pressure metamorphic conditions. Terra Nova 16, 146–151.

Lambert, I.B., Wyllie, P.J., 1972. Melting of gabbro (quartz eclogite) with excess water to 35 kilobars, with geological applications. Journal of Geology 80, 693–708.

Malaspina, N., Hermann, J., Scambelluri, M., Compagnoni, R., 2005. Trace element transfer in the mantle wedge: evidence from polyphase inclusions in garnet-pyroxenites (Dabie-Shan, China). Mitteilungen der Österreichischen Mineralogischen Gesellschaft 150, 100.

Manning, C.E., 1994. The solubility of quartz in the lower crust and upper mantle. Geochimica et Cosmochimica Acta 58, 4831–4839.

Manning, C.E., 1998. Fluid composition at the blueschist–eclogite transition in the model system Na_2O–MgO–Al_2O_3–SiO_2–H_2O–HCl. Schweizerische Mineralogische und Petrographische Mitteilungen 78, 225–242.

Manning, C.E., 2004. The chemistry of subduction-zone fluids. Earth and Planetary Science Letters 223, 1–16.

Massonne, H.-J., 2003. A comparison of the evolution of diamondiferous quartz-rich rocks from the Saxonian Erzgebirge and the Kokchetav Massif: are so-called diamondiferous gneisses magmatic rocks? Earth and Planetary Science Letters 216, 347–364.

McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. Chemical Geology 120, 223–253.

Molina, J.F., Poli, S., Austrheim, H.J.G., Rusin, A., 2004. Eclogite facies vein systems in the Marun-Keu complex (Polar Urals, Russia): textural, chemical and thermally constraints for patterns of fluid flow in the lower crust. Contributions to Mineralogy and Petrology 147, 487–504.

Nadeau, S., Philippot, P., Pineau, F., 1993. Fluid inclusion and mineral isotopic compositions (H–O–C) in eclogitic rocks as tracers of local fluid migration during high-pressure metamorphism. Earth and Planetary Science Letters 114, 431–448.

Nakamura, Y., 1974. The system SiO_2–H_2O–H_2 at 15 kbar. Carnegie Institution of Washington Year Book 73, 259–263.

Nakamura, D., Hirajima, T., 2000. Granulite-facies overprinting of ultrahigh-pressure metamorphic rocks northeastern Su-Lu region, eastern China. Journal of Petrology 41, 563–582.

Nichols, G.T., Wyllie, P.J., Stern, C.R., 1994. Subduction zone melting of pelagic sediments constrained by melting experiments. Nature 371, 785–788.

Patiño Douce, A.E., 2005. Vapor-absent melting of tonalite at 15–32 kbar. Journal of Petrology 46, 275–290.

Patiño Douce, A.E., Mc Carthy, T.C., 1998. Melting of crustal rocks during continental collision and subduction. In: Hacker, B.R., Liou, J.G. (Eds.), When Continents Collide: Geodynamics and Geochemistry of Ultrahigh-Pressure Rocks. Kluwer Academic Pub., Dordrecht, pp. 27–55.

Peacock, S.M., 1996. Thermal and petrological structure of subduction zones. In: Bebout, G.E., Scholl, D.H., Kirby, S.P., Platt, J. (Eds.), Subduction: Top to bottom. Geophysical Monograph. American Geophysical Union, Washington D.C., pp. 119–133.

Perchuk, A.L., Burchard, M., Maresch, W.V., Schertl, H.-P., 2005. Fluid-mediated modification of garnet interiors under ultrahigh-pressure conditions. Terra Nova 17, 545–553.

Philippot, P., 1993. Fluid–melt rock interaction in mafic eclogites and coesite-bearing metasediments — constraints on volatile recycling during subduction. Chemical Geology 108, 93–112.

Philippot, P., Selverstone, J., 1991. Trace element-rich brines in eclogitic veins: implications for fluid composition and transport during subduction. Contributions to Mineralogy and Petrology 106, 417–430.

Philippot, P., Chevallier, P., Chopin, C., Debussy, J., 1995. Fluid composition and evolution in coesite-bearing rocks (Dora-Maira Massif, Western Alps): implications for element recycling during subduction. Contributions to Mineralogy and Petrology 121, 29–44.

Plank, T., Langmuir, C.E., 1993. Tracing trace elements from sediment input to volcanic output at subduction zones. Nature 362, 739–743.

Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediments and its consequences for the crust and mantle. Chemical Geology 145, 325–394.

Poli, S., Schmidt, M.W., 1995. H_2O transport and release in subduction zones: experimental constraints on basaltic and andesitic systems. Journal of Geophysical Research 100, 22299–23314.

Poli, S., Schmidt, M.W., 2002. Petrology of subducted slabs. Annual Review of Earth and Planetary Sciences 30, 207–235.

Rampone, E., Morten, L., 2001. Records of crustal metasomatism in the garnet peridotites of the Ulten Zone (Upper Austroalpine, Eastern Alps). Journal of Petrology 42, 207–219.

Rapp, R.P., Shimizu, N., Normann, M.D., Applegate, G.S., 1999. Reaction between slab-derived melts and peridotite in the mantle wedge: experimental constraints at 3.8 GPa. Chemical Geology 160, 335–356.

Reinecke, T., 1998. Prograde high- to ultrahigh-pressure metamorphism and exhumation of oceanic sediments at Lago di Cignana, Zermatt-Saas Zone, Western Alps. Lithos 42, 147–190.

Rubatto, D., Hermann, J., 2003. Zircon formation during fluid circulation in eclogites (Monviso, Western Alps): implications for Zr and Hf budget in subduction zones. Geochimica et Cosmochimica Acta 67, 2173–2187.

Scambelluri, M., Philippot, P., 2001. Deep fluids in subduction zones. Lithos 55, 213–227.

Scambelluri, M., Piccardo, G.B., Phillippot, P., Robbiano, A., Negretti, L., 1997. High salinity fluid inclusions formed from recycled

seawater in deeply subducted alpine serpentinite. Earth and Planetary Science Letters 148, 485–500.

Scambelluri, M., Bottazzi, P., Trommsdorff, V., Vannucci, R., Hermann, J., Gomez-Pugnaire, M.T., Vizcaino, V.L.S., 2001. Incompatible element-rich fluids released by antigorite breakdown in deeply subducted mantle. Earth and Planetary Science Letters 192, 457–470.

Schmidt, M.W., Poli, S., 1998. Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. Earth and Planetary Science Letters 163, 361–379.

Schmidt, M.W., Vielzeuf, D., Auzanneau, E., 2004. Melting and dissolution of subducting crust at high pressures: the key role of white mica. Earth and Planetary Science Letters 228, 65–84.

Selverstone, J., Franz, G., Thomas, S., Getty, S., 1992. Fluid heterogenities in 2 GPa eclogites: implications for element recycling during subduction. Contributions to Mineralogy and Petrology 112, 341–357.

Sharp, Z.D., Essene, E.J., Hunziker, J.C., 1993. Stable isotope geochemistry and phase equilibria of coesite-bearing whiteschists, Dora-Maira Massif, Western Alps. Contributions to Mineralogy and Petrology 114, 1–12.

Shatsky, V.S., Sobolev, N.V., Vavilov, M.A., 1995. Diamond-bearing metamorphic rocks of the Kokchetav Massif (northern Kazakhstan). In: Coleman, R.G., Wang, X. (Eds.), Ultrahigh Pressure Metamorphism. Cambridge University Press, Cambridge, UK, pp. 427–455.

Shatsky, V.S., Jagoutz, E., Sobolev, N.V., Kozmenko, O.A., Parkhomenko, V.S., Troesch, M., 1999. Geochemistry and age of ultrahigh pressure metamorphic rocks from the Kokchetav Massif (northern Kazakhstan). Contributions to Mineralogy and Petrology 137, 185–205.

Shen, A.H., Keppler, H., 1997. Direct observation of complete miscibility the albite-H_2O system. Nature 385, 710–712.

Sorensen, S.S., 1991. Petrogenetic significance of zoned allanite in garnet amphibolites from a paleo-subduction zone: Catalina Schist, southern California. American Mineralogist 76, 589–601.

Spandler, C.J., 2005. The Geochemical and Petrological Evolution of Subduction Zones: Insights From Blueschist to Eclogite-Facies Rocks from New Caledonia and High-Pressure Hydrothermal Experiments. PhD thesis, The Australian National University, Canberra, 251 pp.

Spandler, C.J., Hermann, J., Arculus, R.J., Mavrogenes, J.A., 2003. Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. Contributions to Mineralogy and Petrology 146, 205–222.

Spandler, C., Hermann, J., Arculus, R., Mavrogenes, J., 2004. Geochemical heterogeneity and element mobility in deeply subducted oceanic crust; insights from high-pressure mafic rocks from New Caledonia. Chemical Geology 206, 21–42.

Stalder, R., Foley, S.F., Brey, G.P., Horn, I., 1998. Mineral-aqueous fluid partitioning of trace elements at 900–1200 °C and 3.0–5.7 GPa: new experimental data for garnet, clinopyroxene, and rutile, and implications for mantle metasomatism. Geochimica et Cosmochimica Acta 62, 1781–1801.

Stalder, R., Ulmer, P., Thompson, A.B., Günther, D., 2000. Experimental approach to constrain second critical end points in fluid/silicate systems: near-solidus fluids and melts in the system albite-H_2O. American Mineralogist 85, 68–77.

Stalder, R., Ulmer, P., Thompson, A.B., Günther, D., 2001. High pressure fluids in the system MgO–SiO_2–H_2O under upper mantle conditions. Contributions to Mineralogy and Petrology 140, 607–618.

Stöckhert, B., Duyster, J., Trepman, C., Massonne, H.-J., 2001. Microdiamond daughter crystals precipitated from supercritical COH+silicate fluids included in garnet, Erzgebirge, Germany. Geology 29, 391–394.

Svensen, H., Jamtveit, B., Yardley, B.W., Engvik, A.K., Austrheim, H., Broman, C., 1999. Lead and Bromine enrichment in eclogite facies fluids: extreme fractionation during lower crustal hydration. Geology 27, 467–470.

Tatsumi, Y., Eggins, S.M., 1995. Subduction Zone Magmatism. Blackwell, Cambridge. 211 pp.

Tenthorey, E., Hermann, J., 2004. Composition of fluids during serpentinite breakdown in subduction zones: evidence for limited boron mobility. Geology 32, 865–868.

Touret, J.L.R., Frezzotti, M.-L., 2003. Fluid inclusions in high pressure and ultrahigh pressure metamorphic rocks. In: Carswell, D.A., Compagnoni, R. (Eds.), Ultrahigh pressure metamorphism. Eötvös University Press, Budapest, pp. 467–487.

Tribuzio, R., Messiga, B., Vannucci, R., Bottazzi, P., 1996. Rare earth element redistribution during high-pressure low-temperature metamorphism in ophiolitic Fe-gabbros (Liguria, northwestern Italy): implications for light REE mobility in subduction zones. Geology 24, 711–714.

Tropper, P., Manning, C.E., 2005. Very low solubility of rutile in H_2O at high pressure and temperature, and its implications for Ti mobility in subduction zones. American Mineralogist 90, 502–505.

Tumiati, S., Thöni, M., Nimis, P., Martin, S., Mair, V., 2003. Mantle-crust interactions during Variscan subduction in the Eastern Alps (Nonsberg–Ulten Zone): geochronology and new petrological constraints. Earth and Planetary Science Letters 210, 509–526.

Ulmer, P., Trommsdorff, V., 1995. Serpentine stability to mantle depths and subduction-related magmatism. Science 268, 858–861.

van Keken, P.E., Kiefer, B., Peacock, S.M., 2002. High-resolution models of subduction zones: implications for mineral dehydration reactions and the transport of water into the deep mantle. Geochemistry Geophysics Geosystems 3, doi:10.1029/2001GC000256.

Widmer, T., Thompson, A.B., 2001. Local origin of high pressure vein material in eclogite facies rocks of the Zermatt–Saas Zone, Switzerland. American Journal of Science 301, 627–656.

Widmer, T., Ganguin, J., Thompson, A.B., 2000. Ocean floor hydrothermal veins in eclogite facies rocks of the Zermatt–Saas Zone, Switzerland. Schweizerische Mineralogische und Petrographische Mitteilungen 80, 63–73.

Wyllie, P.J., Tuttle, O.F., 1960. Experimental investigation of silicate systems containing two volatile components. Part 1: geometrical considerations. American Journal of Science 258, 498–517.

Yaxley, G.M., Green, D.H., 1998. Reactions between eclogite and peridotite: mantle refertilisation by subduction of oceanic crust. Schweizerische Mineralogische und Petrographische Mitteilungen 78, 243–255.

Zack, T., Rivers, T., Foley, S.F., 2001. Cs–Rb–Ba systematics in phengite and amphibole: an assessment of fluid mobility at 2.0 GPa in eclogites from Trescolmen, Central Alps. Contributions to Mineralogy and Petrology 140, 651–669.

Zhang, R.Y., Liou, J.G., Zheng, J.P., 2004. Ultrahigh-pressure corundum-rich garnetite in garnet peridotite, Sulu terrane, China. Contributions to Mineralogy and Petrology 147, 21–31.