The chemical behavior of fluids released during deep subduction based on fluid inclusions

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ABSTRACT

This review combines fluid inclusion data from (HP-)UHP rocks with experimental research and thermodynamic models to investigate the chemical and physical properties of fluids released during deep subduction, their solvent and element transport capacity, and the subsequent implications for the element recycling in the mantle wedge. An impressive number of fluid inclusion studies indicate three main populations of fluid inclusions in HP and UHP metamorphic rocks: i) aqueous and/or non-polar gaseous fluid inclusions (FI), ii) multiphase solid inclusions (MSI), and iii) melt inclusions (MI). Chemical data from preserved fluid inclusions in rocks match with and implement “model” fluids by experiments and thermodynamics, revealing a continuity behind the extreme variations of physico-chemical properties of subduction-zone fluids. From fore-arc to sub-arc depths, fluids released by progressive devolatilization reactions from slab lithologies change from relatively diluted chloride-bearing aqueous solutions (± N\textsubscript{2}), mainly influenced by halide ligands, to (alkali) aluminosilicate-rich aqueous fluids, in which polymerization probably governs the solubility and transport of major (e.g. Si and Al) and trace elements (including C). Fluid inclusion studies point to a reconsideration of the petrological models explaining deep volatile liberation, and their flux into the mantle wedge.
INTRODUCTION

The chemical behavior of fluids in deep subduction zones and its implications for element cycling and flux melting in the mantle wedge, which causes the formation of arc magmas, has been a subject of growing interest in the last twenty years (e.g., Manning 2004; Bebout 2007, 2013). Experimental and theoretical research represents a major tool for understanding the chemical and physical properties of slab-derived fluids, and for modeling the metamorphic evolution of deep subducting rocks (e.g., Ulmer 2001; Poli and Schmidt 2002; Manning 2004; Sanchez Valle 2013; and references cited).

Closely related to theoretical and experimental research are studies of fluid inclusions in metamorphic rocks. High pressure (HP) and ultra-high pressure (UHP) eclogite-facies rocks of crustal origin represent an excellent natural laboratory for the study of subduction-zone fluids, since they underwent pressure and temperature conditions comparable to those hypothesized to occur in deep subducting slabs (Carswell and Compagnoni 2003). A large number of fluid inclusion studies in eclogites and related rocks have reported a remarkable variety of fluid types: aqueous fluids with variable halide content ± non-polar gases (e.g., N₂, CO₂, CH₄), aluminosilicate-rich aqueous fluids, intermediate between silicate melt and water, and hydrous silicate melts (c.f., Scambelluri and Philippot 2001; Touret and Frezzotti 2003; Ferrando et al. 2005; and references cited). Many among these inclusions have lost their original composition, but some still preserve the chemistry of fluid trapped during prograde and peak UHP metamorphic conditions, despite subsequent exhumation from extreme depths. In this paper, we highlight how fluids in inclusions can constrain and explain deep subduction processes. After providing a review of current research on fluid inclusions in (HP-) UHP metamorphic rocks, we express our view on the chemical and physical characteristics of subduction-zone fluids preserved as inclusions, including solvent and element transport capacity, and implications to
cycling of volatiles. Further recent discussion on fluid inclusions in UHP metamorphic rocks can be found in Scambelluri and Philippot (2001), Touret and Frezzotti (2003), Ferrando et al. (2005), Zheng et al. (2011), Klemd (2013), and Hermann et al. (2013).

**FLUID INCLUSIONS IN HP-UHP METAMORPHIC ROCKS**

Fluid inclusions are tiny volumes of mobile volatile-rich phases trapped in minerals during, or after their growth (Roedder 1984). For this reason, they represent the only possible way to acquire firsthand information on naturally occurring fluids. A digest of current main research on fluid inclusions in UHP eclogite-facies metamorphic suites is provided in Table 1. It summarizes different pieces of information, including inclusions’ main textural (stage of trapping, inclusion type, and host minerals) and chemical (daughter minerals, water vs. gas) characteristics, along with the nature of host metamorphic rocks (metamorphic belt, peak P-T conditions, matrix lithologies). A synthetic report of the interpretations proposed by the single authors is included. Most examples are on primary fluid inclusions (i.e., fluid inclusions trapped during growth of the host mineral; Roedder 1984) in peak metamorphic minerals of crustal rocks, that, as a consequence, preserve the composition of the hydrous fluid phases released by the slab at more than 90 km depth, during deep subduction (i.e., P-T stability field of coesite).

Three distinct populations of fluid inclusions are observed in HP and UHP metamorphic rocks (Table 1): i) chloride-bearing aqueous and/or non-polar gases fluid inclusions (FI), ii) multiphase solid inclusions (MSI), and iii) melt inclusions (MI). We will deliberately be avoiding the term ‘polyphase inclusion’ often reported in literature as an alternative to MSI (see, Table 1), since this definition applies to any inclusion containing...
more than two phases (e.g., a fluid inclusion containing liquid H₂O, liquid CO₂, and gaseous
CO₂ is defined as a polyphase inclusion) and may cause confusion.

**Chloride-bearing aqueous, and/or non-polar gaseous fluid inclusions (FI)**

Chloride-bearing aqueous fluid inclusions (FI) are observed in HP and UHP eclogite
(Svensen et al. 1999, 2001; Xiao et al. 2000, 2002; Fu et al. 2001; Shen et al. 2003; Ferrando et
al. 2005a; Mukherjee and Sachan 2009), eclogitic veins and segregations (Philippot and
Selverstone 1991; Selverstone et al. 1992), quartzite and whiteschist (Philippot et al. 1995;
Ferrando et al. 2009), Mn-rich garnet nodules (Frezzotti et al. 2011), and garnet pyroxenite (Fu
et al. 2003a; Table 1). FI are small (< 40-50 μm in diameter) and show irregular, rounded, or
negative crystal shapes. Although some biphase (liquid + vapor) liquid-rich FI are reported (e.g.,
Ferrando et al. 2005b), most of them are three-phase (solid + liquid + vapor) inclusions with
about 40-90% of the total volume consisting of liquid + vapor (Figs. 1b - d).

As evident from Table 1, one (e.g., halite) to three chlorides are generally observed (Fig.
1c), often associated with carbonates (e.g., calcite, Mg-calcite, dolomite, hydrous carbonates),
and/or minor sulfates (mainly gypsum), sulfides (mainly pyrite), and oxides (rutile, ilmenite).
More rarely, phosphate (apatite, monazite) and silicate (amphibole, mica, epidote, quartz,
feldspars, kyanite, omphacite, ellenbergerite, glaucophane; Fig. 1d) daughter minerals have been
described. Interestingly, FI in garnet nodules from Lago di Cignana (Italian western Alps)
contain several carbon phases (carbonate, diamond, graphite, carbonaceous material) and an
aqueous fluid bearing HCO₃⁻, CO₃²⁻, and SO₄²⁻, ions, and silica monomers in solution, but no
chlorides (Fig. 1b).

Non-polar gaseous fluid inclusions are observed in eclogite (Fu et al. 2001; Xu et al.
2006; Mukherjee and Sachan 2009) and garnet pyroxenite (Fu et al. 2003a; Table 1). These tiny
inclusions (< 10 μm in diameter) are single-phase pure (N₂, or CH₄) or binary (N₂-CH₄, rarely CO₂-N₂) mixtures, gray to dark in color due to their low refractive index. Commonly, they are associated with chloride-bearing aqueous fluid inclusions (Fu et al. 2001). Mixed N₂-CO₂-CH₄-H₂O ± solids inclusions (Fig. 1a) are reported from HP eclogite (Fu et al. 2003b; Xiao et al. 2001, 2002), garnet pyroxenite (Fu et al. 2003a), quartzite (Frezzotti et al. 2007), and whiteschist (Philippot et al. 1995; Table 1). The gas bubble volume is variable from < 20 to > 80 % of the inclusion. These inclusions occur isolated (Frezzotti et al. 2007), or in association with chloride-bearing aqueous fluid inclusions (Fu et al. 2003a). Halite is the most common mineral phase in these inclusions, although gypsum, anhydrite, and pyrite have been locally reported (Table 1).

Multiphase solid inclusions (MSI)

Multiphase solid inclusions (MSI; Table 1) are peculiar primary inclusions present in peak mineral assemblages of UHP rocks, recognized in eclogite (Ferrando et al. 2005 a, 2005b) and eclogitic veins (Zhang et al. 2008), felsic gneiss (Stöckhert et al. 2001, 2009; Dobrzhinetskaya et al. 2003a, 2003b, 2012), quartzite (Frezzotti et al. 2007; Ferrando et al. 2005b), Grt-Cpx-Qtz rocks (Hwang et al. 2003), whiteschist (Philippot et al. 1995; Ferrando et al. 2009), marble (Hwang et al. 2005, 2006), garnet pyroxenite (van Roermund et al. 2002; Carswell and van Roermund 2005; Vrijmoed et al. 2008; Malaspina et al. 2010), garnet peridotite (Malaspina et al. 2006, 2009), and Ol-Opx rocks (Scambelluri et al. 2001).

MSI show variable sizes (from 5 to ca. 100 μm in diameter), and polygonal or negative crystal shapes (Figs. 2 and 3). At room temperature, they consist of aggregates of 4 to 10 different solid phases of relatively large sizes, with subordinate fluid, or empty cavities (< 40% of the total volume of the inclusions; Figs. 2a and 2b). Most of the solid phases are hydrous (alkali) aluminosilicate minerals (white micas, talc, chlorite, phlogopite, biotite, amphiboles, epidote s.l.,
ellenbergerite, staurolite), though anhydrous silicates (quartz, feldspars, zircon, kyanite, pyroxenes, titanite, olivine, kalsilite) are also observed (Table 1). Carbonates (mainly calcite, Mg-calcite, dolomite, magnesite) constitute common, subordinate phases. Minor sulfates (mainly gypsum and anhydrite), or sulfides (mainly pyrite), phosphates (mainly apatite and monazite), and oxides (mainly rutile and spinel s.l.) can also be present (Table 1). Reduced carbon phases (diamond, graphite, disordered carbonaceous material) are observed in some localities (Stöckhert et al. 2001; van Roermund et al. 2002; Dobrzhinetskaya et al. 2003a, 2003b, 2012; Carswell and van Roermund 2005; Vrijmoed et al. 2008; Stöckhert et al. 2009; Malaspina et al. 2010; Table 1) Chlorides are rarely present (Philippot et al. 1995; Hwang et al. 2005, 2006; Ferrando et al. 2009; Table 1).

In MSI, the relatively large solid phases, in particular lamellar minerals, show intimate intergrowths and preferred orientations, often resulting from periodic crystallization (Figs. 2a, 2c, 2d, and 3). Textural relationships of daughter minerals are different from those observed in crystallized MI in plutonic and in HT metamorphic rocks (i.e., “stone cavities” in granites, and “nanogranites” in migmatites; Sorby 1858; Frezzotti 1992; Cesare et al. 2009). In MSI, crystallization of daughter phases appears to have started in the center of the inclusion cavity and proceeded to the walls, exponentially increasing mineral surface. Crystallization seems to have occurred from a homogeneous relatively low-viscosity melt or fluid, by processes such as diffusion mass transport and growth (e.g., periodic precipitation; Liesgang phenomena). Locally, granoblastic textures, and rare developments of triple joints among equant and prismatic minerals are also observed (Figs. 2b).

In contrast to the previous class of FI, it is difficult to optically detect liquid water in MSI (Figs. 2 and 3) due to: i) the high amount of solid phases in the inclusions, ii) the high density of the trapped fluids, and iii) the possibility that water passively diffused from inclusions during the retrograde evolution of the host rocks (see following paragraphs). Microthermometric analyses
collected in MSI with a relatively high amount of fluid indicate a solute-rich aqueous solution (e.g., Zhang et al. 2005). Non-polar gas species, such as N₂ and/or CO₂ have not been detected by Raman microspectroscopy (Table 1).

Melt inclusions (MI)

Melt inclusions (MI) can occur in quartz-feldsparic rocks and garnet-bearing gneiss (Hwang et al. 2001, 2006; Mposkos et al. 2009), metapelites (Lang and Gilotti 2007), Grt-Cpx rocks (Hwang et al. 2004, 2005), marble (Korsakov and Hermann 2006), eclogite (Shen et al. 2003; Gao et al. 2012), garnet peridotite (Naemura et al. 2009; Table 1). They form by decompression melting of eclogite-facies matrix rocks during early retrogression, or by local in-situ dehydration-melting of hydrous mineral phase inclusions within prograde and peak minerals (see also, Klemd 2013).

In general, MI in UHP metamorphic rocks are recrystallized, similarly to what observed in plutonic or in HT metamorphic rocks, although, most unexpectedly, minor volumes of glass have been reported in a few cases (e.g., Hwang et al. 2004; Hwang et al. 2006; Table 1). During slow cooling in the Earth’s crust, crystallization of silicate phases inside MI typically initiates on the cavity wall, and the nucleation rate is greater than the growth rate, resulting in the formation of a number of randomly-oriented fine-grained, anhedral to subhedral crystals of similar size (Fig. 4; Frezzotti 2001). In UHP rocks, MI are generally small (ca. 10-50 µm in diameter), with polygonal or negative crystal shapes, generally filled by tiny aggregates of feldspars, micas, and quartz, or, more rarely, of carbonates, and carbon phases ± silicates (Table 1). In particular, these inclusions show magmatic textural relationships, such as an order of crystallization, or graphic intergrowths (e.g., Korsakov and Hermann 2006; Mposkos et al. 2009), similar to (crystallized) MI in plutonic and HT metamorphic rocks. Fine-grained mineral assemblages are also observed...
to partly or totally replace former phengite lamellae because of their *in-situ* dehydration melting (e.g., Gao et al. 2012; Liu et al. 2013). Finally, irregular pockets filled by relatively coarse-grained reactants and products of dehydration melting reactions involving phengite are also reported in UHP rocks (Lang and Gilotti 2007).

**POST-ENTRAPMENT MODIFICATIONS OF HP-UHP FLUID INCLUSIONS AND MULTIPHASE SOLID INCLUSIONS**

UHP FI and MSI are usually trapped during the growth of the host mineral (primary or early inclusions; Roedder 1984; Touret 2001). They occur isolated or as clusters and, if abundant, they are regularly distributed (Fig. 5a) marking the growth zones of the host mineral (Fig. 5b). The fidelity of the FI and MSI fluid record is based on two fundamental assumptions. The first one is that their chemistry must be representative of the composition of the fluid phases present in the system at trapping conditions (Roedder, 1984). Because of the constant proportions of crystallized minerals (Fig. 2 and 3), most FI and MSI appear to have trapped an homogeneous UHP fluid phase. Exceptions, are represented by those inclusions which contain incidentally-trapped minerals. These last ones are recognizable for their nonsystematic occurrence and, typically, for having larger dimensions than daughter minerals (Fig. 5c).

Similarly, in MI, presence of magmatic mineral assemblages, replacing a hydrous phase during its *in-situ* dehydration melting, and/or of reactants and products of a dehydration melting reaction are a strong evidence for incipient anatexis of UHP rocks, but are not representative for the composition of the melt generated during this event.

The second assumption requires that, after trapping an homogeneous fluid phase, inclusions behaved as closed systems, i.e. they evolved independently from the host minerals.
Post-trapping modifications can affect some inclusions and spare some others nearby (Fig. 6). This depends on the nature of the host mineral, and on the size, shape and location (i.e., dislocations in the host) of the inclusions in the host mineral (Viti and Frezzotti 2000; 2001; Touret 2001; Frezzotti and Ferrando 2007; Stöckhert et al. 2009).

As illustrated in Fig. 7, crystallization of daughter minerals (stage 2 of Fig. 7) during decompression does not necessarily imply changes in the chemical composition of the former fluid. In some cases, also the retrograde chemical interaction between the inclusion and the host mineral does not affect the chemical composition of the former fluid. For example, the negative crystal shape shown by most inclusions (Figs. 2, 3 and 6) develops just after the entrapment by dissolution and precipitation of the host mineral on the inclusion walls (stage 2 of Fig. 7). This is an equilibrium process that is not considered to modify the former fluid composition (e.g., Roedder 1984; van den Kerkhof and Hein 2001; Frezzotti 2001). Similarly, retrograde metamorphic reactions inside MSI (e.g., pseudomorphosis, hydration reactions; Figs. 6 or 8a, respectively; stage 4 of Fig. 7) do not change the chemistry of the former fluid (Frezzotti et al. 2012a).

In contrast, non-equilibrium growth of the host mineral on the inclusion walls (typically with slightly different composition) can modify the chemical composition of both the trapped fluid and the host mineral that crystallizes on the inclusions walls (e.g., Heinrich and Gottschalk 1995; Frezzotti 2001). This evolution is commonly observed in MSI (and MI) which were subject to high-$T$ conditions during the retrograde evolution (stage 3 of Fig. 7). Retrograde metamorphic reactions between the host mineral and the inclusions on cooling (e.g., hydration reactions) and diffusion of elements from the inclusions, can modify significantly the composition (Fig. 8a and d), and changes in the oxygen fugacity of the inclusion fluid may also occur. Chemically re-equilibrated MSI (Fig. 6 and 8c-f) are easy to recognize, since they show irregular contours typically forming re-entrant angles, and can contain newly formed minerals.
Due to the strong decompression during retrograde evolution, decrepitation (i.e., burst by explosion) represents another very common post-trapping process in both FI and MSI. This process modifies the former density of the fluid. Decrepitation occurs when the host mineral is no more able to accommodate the pressure difference in and out of the inclusion ($\Delta P = P_{\text{in}} - P_{\text{out}}$ >> 0; Fig. 7) (e.g., Touret 2001; Franz et al. 2001; Stöckhert et al. 2009). FI in elogite-facies rocks can re-equilibrate their density at different $P$-$T$ conditions several times during decompression (Fig. 7; e.g., Touret 2001; Touret and Frezzotti 2003; Frezzotti and Ferrando 2007; Stöckhert et al. 2009).

In MSI, early UHP-HP retrograde decrepitation (stage 3 of Fig. 7) can be identified by irregular contours and short and large fractures (offshoots) departing from the inclusion corners (Figs. 6, 8a, 8e, 9a, 9c, 9d), similarly to fluid inclusions in mantle xenoliths (Fig. 9b). On the contrary, decrepitation at lower $P$ (stage 5 of Fig. 7), liberating a fluid phase when all minerals have already crystallized (stage 4 of Fig. 7), generally forms: i) star-shaped contours (Figs. 6, 9d-e), and/or ii) haloes of very small FI distributed around the inclusion (Fig. 9c), and/or iii) short trails of tiny secondary FI lining from the decrepitated inclusions (Fig. 8c-d). These petrographic features are similar to those observed in volatile-rich MI in plutonic rocks, undergoing volatile oversaturation and magma degassing during slow cooling after trapping as inclusions (Fig. 9f).

**ELUSIVE AND FUGITIVE WATER**

A careful petrographic study is necessary to select those UHP inclusions potentially representative for the chemical composition of the metamorphic fluids. The determination of the
water content of the former fluids is more problematic. In most MSI, water represents an elusive and fugitive component, although empty spaces between hydrous daughter minerals (Fig. 8a) testify for the (former) presence of an aqueous fluid component. A valuable way to study water speciation inside MSI is by spectroscopic techniques. One possible analytical approach is described in Frezzotti et al. (2010). In Fig. 10, synchrotron FT-IR maps show the speciation of water in MSI both as H$_2$O molecules (Fig. 10b) (i.e., liquid phase; absorption bands in the 3000–3500 cm$^{-1}$ region, Fig. 10e), and as OH$^-$ groups (Fig. 10c) (i.e., in daughter mineral phases; absorption bands in the 3500–3800 cm$^{-1}$ region, Fig. 10e). Comparing Figs. 10a and 9b, the systematic absorption increase in the 3000–3500 cm$^{-1}$ region in correspondence of MSI reveals that, in contrast with the optical observation, they may contain some liquid water. Quantitative analyses, however, are not possible.

An additional concern is that the low-water content of MSI could result from passive H$_2$O diffusion during the retrograde $P$-$T$ evolution. MSI can exchange H$_2$O with the host minerals if the internal $P_{\text{H}_2\text{O}}$ in the inclusion is higher than the external $P_{\text{H}_2\text{O}}$ (or $X_{\text{H}_2\text{O}}$) of the fluids circulating in the rocks (Sterner and Bodnar, 1991), a very common case during retrograde decompression at relatively high temperatures (Fig. 7). If decrepitation does not occur, the inclusion fluid $P_{\text{H}_2\text{O}}$ can passively re-equilibrate with the external fluid conditions. Identifying MSI dehydration, if present at all, would also require spectroscopic investigations. The example in Fig. 10d shows a synchrotron FT-IR map of hydrogen distribution in pyrope (Frezzotti et al. 2012a and b). Exponential enrichment of bonded hydrogen in garnet approaching MSI reveals the change from molecular water in MSI to OH$^-$ bonds to the anhydrous host. Hydrogen gradients, recorded by symmetrically different colored haloes, represent actual water content variations in garnet, with the exception of the MSI area where the extremely high water concentration in garnet in part results from a MSI contribution (yellow to pink haloes in Fig. 10d). Fluid inclusion “dehydration” processes were previously proposed to interpret the origin of some pure CO$_2$ FI in peridotite xenoliths, formed at depths of about 60 - 80 km and rapidly
brought to the surface by erupting magmas (Hidas et al. 2010; Frezzotti et al. 2012a). In these rocks, thermodynamic modeling (MFSHC system) of observed reactions between FI and surrounding minerals suggested a potential H$_2$O content in mantle C-O-H fluids variable from 10 to 50 mole %, lost from FI after trapping in minerals (Frezzotti et al. 2012a).

These results suggest that the amount of fugitive water from inclusions formed at high $P$-$T$ conditions may not be trivial, and that MSI could have contained tens of mole % H$_2$O, most of which - if not all - potentially lost during early retrograde decompression in matrix rocks. Extending this process to FI, we hypothesize that some of the highly saline compositions described in the previous paragraphs (e.g., Fu et al. 2001; Ferrando et al. 2005a; Zhang et al. 2005; Xiao et al. 2006; Mukherjee and Sachan 2009), could also result from selective H$_2$O loss during exhumation. The relatively low density of these brine FI (i.e. large vapor/liquid ratios; Fig. 1a and c) seems to support a retrograde FI dehydration trend.

FLUIDS IN DEEP SUBDUCTION ZONES

**Chemical composition of fluids released during deep subduction**

HP and UHP fluids released during subduction have a profound petrological and geochemical action both in the control of some state variables (first of all $P_{H_2O}$), and in the dissolution and transport of chemical components from the slab by inducing metasomatic addition to the mantle wedge. Diverse fluid compositions are preserved in prograde and peak metamorphic phases of deeply subducted rocks: water-dominated C-O-H-N mixtures (e.g. Klemd 1989; 2013; Giaramita and Sorensen 1994; Vallis and Scambelluri 1996; El-Shazly and Sisson 1999; Franz et al. 2001; Gao and Klemd 2001), brines, N$_2$-CO$_2$/CH$_4$ fluids (e.g., Andersen et al. 1989; Selverstone et al. 1992; Philippot 1993; Klemd et al. 1992, 1995; Scambelluri et al. 1997, 1998; Xiao et al. 2000, 2002; Fu et al. 2001, 2002, 2003; Mukherjee...
and Sachan 2009), aluminosilicate-rich aqueous fluid phases (e.g., Ferrando et al. 2005 and
references cited), and, more rarely, hydrous melts.

Early studies by Philippot et al. (1995) first described a relevant variation in the
chemistry of fluids passing from prograde HP to peak UHP metamorphic conditions in
coesite-pyrope-bearing whiteschists from the Dora-Maira massif (Italian Western Alps). They
noted that large quantities of dehydration fluids released during prograde metamorphism -
predating pyrope and coesite UHP assemblage - were preserved as low-solute aqueous FI in
relic kyanite within pyrope. Further evidence for dehydration fluids at UHP conditions,
attending the growth of garnet, was given by MSI in pyrope, which contain phyllosilicates,
Mg-phosphate, chlorides, and opaques, but no optically-visible aqueous fluid. Over time, fluid
inclusion research combined with petrological investigations further demonstrated that water-
rich fluids with variable halide contents (± N2 and CH4/CO2) generally dominate in HP
prograde, low-T UHP peak, and early retrograde metamorphic mineral assemblages, whereas
complex aluminosilicate-rich aqueous fluid phases are typically preserved in UHP peak
metamorphic mineral assemblages at T above about 600-650°C.

In the following sections, we provide a synthesis of the current knowledge on the
chemical composition of fluids in deep subduction zones, based on fluid inclusion literature
summarized in Table 1. We concentrate on those eclogite-facies rocks of crustal origin
equilibrated at P-T conditions relevant for slabs at sub-arc depths (i.e., coesite facies; 2.5-4
GPa).

Aqueous fluids ± N2

In some eclogite-facies rocks from Caledonian, Hercynian, and Alpine L.T-HP, and -
UHP metamorphic terranes, the prograde, peak, and early retrograde fluid composition within
different rock types is uniform in terms of H2O, which represents the main component, but
variable in terms of solutes, and non-polar components (N₂ contaminated by CO₂, or CH₄), as
previously summarized by Scambelluri and Philippot (2001), Touret and Frezzotti (2003),

FI studies in eclogites from the Alps indicate that prograde aqueous fluids contain
mainly NaCl and MgCl₂, with only subordinate concentrations of CaCl₂ and KCl. Calculated
salinities vary from about 3 to 50 in NaCl equivalent wt. % (e.g., Philippot and Selverstone
1991; Selverstone et al. 1992; Philippot et al. 1995; Scambelluri et al. 2001). To explain the
Na-, and Mg-dominated nature of such HP chloride-bearing solutions, two processes have
been proposed: recycling of sea-water (Scambelluri et al. 1997), or hydrothermal alteration of
presented a model for the generation of mobile high-MgCl₂ aqueous plumes at mantle depths,
via breakdown of subducted serpentinites.

In the Dabie-Shan and Sulu UHP eclogite-facies continental rocks, prograde and early
retrograde metamorphic fluids preserved within FI are generally CaCl₂-dominated (Xiao et al.
2000, 2001; Fu et al. 2001, 2002, 2003; Zhang et al. 2005; Frezzotti et al. 2007), and not
NaCl-rich as in oceanic rocks. Xiao et al. (2000) and Fu et al. (2001, 2003) reported also the
presence of N₂ ± CO₂, or CH₄-rich HP fluids. In matrix rocks, the scale of fluid chemical
heterogeneity is extremely variable. For example, in metasediments and eclogites from the
Dabie-Shan UHP terrane, aqueous fluids have different salinities and, most importantly,
different cations in solution, even at the scale of the crystal (Fu et al. 2002). In these fluids,
the nature of cations is related to the host mineral phase (e.g. Ca-dominated chlorides in
epidote, and Na-, K-chlorides in amphibole). Fluid chemical variability indicates very limited
fluid transport before trapping as inclusions, and generally supports an internal origin. Based
on the very low δ¹⁸O of minerals containing FI in eclogite-facies continental rocks from
Dabie-Sulu, Fu et al. (2002, 2003), Ferrando et al. (2005a), and Frezzotti et al. (2007)
proposed an ultimate origin from past meteoric water brought to mantle depths (e.g., Zhang et al. 2011, and references cited).

Besides chlorine and alkalis, additional minor solutes in aqueous fluids are Si, Al, Ti, C, and S species. The aluminosilicate content in aqueous fluids increases with increasing pressure, while chlorine shows the opposite trend. For example, prograde fluids formed at about 2.5 GPa and 600°C in the Dora-Maira whiteschists contain Cl, Mg, alkalis, with subordinate Si and Al (i.e., Na- and Mg-chlorides and paragonite as daughter phases in FI; Philippot et al. 1995; Ferrando et al. 2009). At 3.5 GPa and similar temperatures (600°C), peak aqueous fluids in UHP metasediments from Lago di Cignana, also in W Alps, contain dominantly Si, Al, Ti, C, Ca, and alkalis (e.g., quartz, rutile, paragonite, carbonate and diamond as daughter phases in FI; Frezzotti et al. 2011; 2014), while Cl appears as a very subordinate component.

From Table 1, calculated solute contents in FI range from less than 3 up to 50 wt. % in NaCl equivalent. Experiments and thermodynamic modeling suggest that aqueous fluids formed at depths below about 90 km are diluted solutions (< 20 wt. % in NaCl equivalent; e.g., Manning 1998; Kessel et al. 2005a; Hermann and Spandler 2008; Spandler and Picard 2013; and references cited). Considering that many HP aqueous fluids contain less than 30 wt. % solutes (cf., Table 1), most researchers have interpreted the inclusion fluid record to confirm a dominantly diluted nature of HP aqueous subduction-zone fluids. Fluid-fluid immiscibility processes (Newton and Manning 2010), or passive solute enrichment due to water loss from inclusions, could have brought to the extreme chloride enrichment observed in some FI.

HP-UHP FI highlight also the possible presence of non-polar fluid species, such as N2, CO2, and CH4, although this last one is more commonly formed during early decompression (cf., Table 1; Xiao et al. 2000, 2002; Fu et al. 2001, 2002, 2003a, 2003b; Yang et al. 2001). N2
is by far the most abundant non-polar gas in prograde and peak metamorphic fluids (cf., review by Touret 2001; Frezzotti and Touret 2003; Klemd, 2013). Up to 20 mole % N₂ were measured in HP aqueous fluids in eclogites from western Norway, where eclogitization is triggered by channeled fluids in shear zones (Austreheim 1987; Andersen et al. 1989; 1990; 1993). Although the thermodynamic properties of the C-O-H-N system are not fully known, it is possible to trace the transition from HP to UHP conditions of aqueous fluids containing nitrogen. Since the binary system H₂O - N₂ system shows a miscibility gap at P > 2-2.2 GPa at temperatures ≤ 700°C (X₅₂ > 0.2; Haefner et al. 2002), H₂O-N₂ fluids formed in the P-T stability field of coesite are expected to be immiscible, while full H₂O-N₂ miscibility should be expected at lower pressures.

N₂ fluids can form by release of ammonium (NH₄⁺) substituting for K⁺ in micas, during prograde dehydration with increasing metamorphism (Hallam and Eugster 1976; Duit et al. 1986; Haendel et al. 1986; Bebout and Fogel 1992; Bebout, 2013). The speciation of nitrogen in C-O-H-N fluids depends on pressure, temperature, fluid composition, and is probably controlled by redox conditions (Andersen et al. 1993; Pöter et al. 2004). It has been shown, that, during cold subduction, almost the complete budget of nitrogen can remain in micas up to 2.5 GPa (Busigny et al. 2003). In addition, boron nitride (BN) and osbornite nitrides (TiN) inclusions in coesite have been reported at higher pressures (Dobrzhinetskaya et al. 2008).

*(Alkali) aluminosilicate-rich aqueous fluids*

MSI in UHP subduction rocks (P > 3GPa), formed at peak metamorphic temperatures above about 600°C, typically consist of several hydrous (alkali) aluminosilicates, such as paragonite, muscovite, chlorite, and phlogopite, and variable amounts of anhydrous and hydrous sulfates, carbonates, phosphates, chlorides, and (former) H₂O (Table 1; Figs. 2, 3, and 6). Over the last decade, the growing interest on these volatile-rich microsystems induced
to an increase of research and discussion to understand the composition and the properties of
the fluid media that were originally trapped. From the compilation of data on daughter
minerals in MSI, it is evident that Si, Al, and alkalis, but not halides, are the major
constituents of UHP water-rich fluid phases preserved in MSI. Element solubility appears
distinct from an aqueous fluid phase at crustal depths (cf., Yardley 2013). Deep subduction
fluids contain far too much Al2O3 and SiO2, which are known to have very limited solubility
in water at crustal conditions, irrespective of salinity. Nonetheless, these water-rich phases
have major element contents that do not resemble any silicate melts of magmatic composition,
generated by volatile-saturated partial melting of metasedimentary or eclogitic rocks at high
metamorphic grades.

A reconstruction of the major element composition of UHP water-rich phases has been
attempted by Ferrando et al. (2005, 2009), and Frezzotti et al. (2007) averaging the vol. % of
daughter minerals in MSI (EMPA analyses; for the procedure see Ferrando et al. 2005). The
method suffers of uncertainties, in part due to the processes that may have affected inclusions
during retrograde decompression, including chemical interaction with the host mineral phase
(Heinrich and Gottschalk 1995; Svensen et al. 1999; Franz et al. 2001). Nevertheless, semi-
quantitative analyses are sufficient for petrological investigations and provide constrains on
the major element composition of water-rich phase released during deep subduction.

There is an evident link between the nature of chemical species present in UHP fluids
and the chemistry of the matrix metamorphic rocks which undergo progressive
devolatilization reactions. A nice example is represented by the composition of inclusion
fluids in UHP eclogite-facies metamorphic series from the Sulu terrane, which consist of both
sedimentary and igneous lithologies attaining the same P-T conditions (3.5 GPa, 750 °C). In
UHP quartzite (phengite and epidote s.l. not stable) reconstructed peak fluid compositions
indicate major SiO2 (24 wt.%), Al2O3 (30 wt.%), CaO (9 wt.%), K2O (5 wt.%), Na2O (3
wt.%), and SO₃ (11 wt.%), with subordinate TiO₂, Fe₂O₃, FeO, MgO, BaO, P₂O₅, Cl⁻, F, and (CO₃)²⁻. In eclogites, fluids have similar SiO₂ (26 wt.%), Al₂O₃ (20 wt.%), and CaO (7 wt.%), but considerably higher MgO (4 wt.%), FeO(Ct) (FeO = 6 wt.% Fe₂O₃= 4 wt.%), and P₂O₅, and almost no alkalis, carbonates, and sulfates. More evidence supporting that UHP aqueous phases can dissolve rock components can be found in the chemistry of fluids formed during the growth of the large pyropes in Dora-Maira metasomatic whiteschists (phlogopite and talc not stable; phengite stable; 4 GPa, 700 °C), which contain high MgO (25.5 wt%), SiO₂ (29 wt%), and Al₂O₃ (23 wt%), while extremely subordinate Fe₂O₃ (4.7 wt%), S (3.2 wt%), Na₂O (1.3 wt%), CaO (0.6 wt%), P₂O₅ (0.4 wt%), and K₂O (0.2 wt%).

A minimum water content of about 20 wt. % has been calculated considering the amount of water bonded in daughter hydrous minerals in MSI, and hypothesizing that the void volume between different daughter phases originally contained H₂O with a density of 1.3 g/cm³ (cf., Ferrando et al. 2005 and references cited; Fig. 2, 3, 8, and 9). The original water content of deep subduction fluids, however, should have been considerably higher, perhaps in the order of 40-60 wt. %, in part lost by passive H₂O diffusion from inclusions during retrogression. Chlorine contents are low, below a few unit wt. %, and CO₂, N₂ and CH₄ have not been detected (e.g., Raman spectroscopy analyses).

Extending the examples discussed above with literature data in Table 1 shows that progressive devolatilization reactions in rocks control the chemistry of aqueous fluids released during deep subduction, depending on rock composition and P-T subduction path, as predicted by theoretical and experimental petrology (e.g., Schmidt and Poli 1998, 2003; Hermann 2002a; Hacker et al. 2003; Hermann et al. 2006). As illustrated in Figure 11, the breakdown of phengite governs the alkali enrichment observed in alkali aluminosilicate aqueous fluid phases in Sulu metasediments, while the Mg-enriched nature of Dora-Maira
UHP fluids derives from phlogopite and talc breakdown in these metasomatic rocks of crustal origin.

In summary, the emerging feature from FI and MSI studies (Table 1) is that at HP conditions, subduction zone fluids are relatively dilute aqueous solutions (± non-polar gases), containing chlorides, alkalis, Si, and Al, with properties similar to crustal aqueous fluids. At greater sub-arc depths, fluids released by crustal lithologies contain increasing amounts of alkali aluminosilicate components ± carbonates phosphates, and sulfates/sulfides, while halides do not appear anymore more as the principal ligands. Thus, although we must acknowledge the limitations of quantitative major element analyses in FI and MSI, observed chemical variations provide key insights into element solubility in deep-subduction aqueous fluids, which results from major structural variations, as it will be discussed in the next section.

Experimental approach: Structure and solvent capacity of HP/UHP fluids

Knowledge of deep subduction-zone fluids behavior implicitly demands for thermodynamic models. When considering the chemical composition of FI and MSI, it is clear that water is the relevant volatile at sub-arc depths. However, water-rich phases containing a great silicate concentration (i.e., MSI) have properties which are intermediate between those generally attributed to aqueous fluids and to hydrous silicate melts, an obvious avenue for experiments and theoretical models.

Experimental and theoretical studies on quartz solubility in water have shown that at high pressure, the silica content of aqueous fluids rises considerably, and the silica-saturated fluid phase and the water-saturated melt progressively approach each other (Fig. 12; Newton & Manning 2008; Mysen 2010; Dolejš and Manning 2010; Hunt and Manning 2012). In the
SiO$_2$-H$_2$O system, immiscibility between melt and fluid vanishes at the upper critical endpoint (point C in Fig. 12), as aqueous fluids form a single continuous solution with silicate melts (Kennedy et al. 1962; Anderson and Burnham 1965; Paillat et al. 1992; Ryabchikov 1993; Bureau and Keppler 1999; Newton and Manning, 2008; Stalder et al. 2000, 2001). The $P$-$T$ location of the upper critical endpoint for the SiO$_2$-H$_2$O system was determined at 1 GPa and 1080°C by Kennedy et al. (1962) and Anderson and Burnham (1965). In natural systems, the $P$-$T$ conditions of the upper critical endpoint depend on the chemistry of the silicate system. For example, they correspond to 2 GPa and 700 °C for the NaAl-Si$_3$O$_8$–H$_2$O system (Paillat et al. 1992; Stalder et al. 2000). For more complex systems, such as basalt-H$_2$O, Ca-bearing granite-H$_2$O, haplogranite-H$_2$O, jadeite-H$_2$O, nepheline-H$_2$O, supercritical $P$-$T$ conditions have been proposed at pressures variable from 3.4 to 6.0 GPa, with currently no general consensus (for discussion cf., Eggler and Rosenhauer 1978; Ryabchikov 1993; Bureau and Keppler 1999; Mysen and Shang 2003; Mibe et al. 2011).

Based on thermodynamics, the nature of UHP fluids in subduction zones has been discussed at great length in the literature, and several definitions have been applied: intermediate fluids (Manning 2004; Frezzotti et al. 2007; Ferrando et al. 2009), supercritical liquids (Schmidt et al. 2004; Kessel et al. 2005b; Mysen 2012; Spandler and Pirard 2013), supercritical fluids (Ferrando et al. 2005a; Malaspina et al. 2006; Hack et al. 2007a; Liebscher 2010; Zhang et al. 2011; Zheng et al. 2011; Kawamoto et al. 2012), supercritical hydrous melts and transitional fluids (Hermann et al. 2006, 2013). Recently, Sanchez-Valle (2013) proposed to adopt the term fluid for any water-rich phases released in subduction zones at sub-arc depths, since: “the meaningful distinction of liquid, vapor, gases at ambient conditions becomes obsolete at high pressures and temperatures where transitions between the various fluid types are often gradational.”
At high pressure and temperature conditions, the (supercritical) fluid vs. melt vexata quaestio is more a semantic than a petrological controversy. As summarized by Hack et al. (2007b) most subduction geothermal gradients are likely to reach P-T conditions close or above the upper critical endpoints of most crustal lithologies. Thus, during deep subduction, the hydrous solidus should be seen as a convenient temperature boundary at which the concentration of silicate components dissolved into aqueous fluids progressively increases, without the abrupt chemical changes resulting at crustal P-T conditions (cf., Fig. 11).

FI and MSI demonstrate beyond reasonable doubt the relevant and gradual increase of the (alkali) aluminosilicate solute load, without phase change, predicted in model fluids by thermodynamics at increasing P (Fig. 12; e.g., Bureau and Keppler 1999; Hunt and Manning 2012). For example, at depths greater than about 90-100 km (P ≥ 3.2 GPa) with transport to UHP conditions with little concomitant heating (T=600°C), water dominates over alkali aluminosilicate solutes in released fluids (Fig. 12; FI in UHP rocks from Alps). At higher P and sub-magmatic temperatures (P = 3.4-4 GPa; T = 700-800°C), approaching the hydrous solidus for sedimentary and granitic rocks, aqueous fluids record an increase of solubility of Si, Al, and alkalis by at least a factor of ten, reaching about 50-60 wt. % solutes (Fig. 12; MSI in UHP rocks from Alps and Dabie Shan-Sulu). Fluids released at extremely high P and T (about 5-8 GPa, and 900°C; Kokchetav Massif; Dobrzhinetskaya et al. 2003a; Hwang et al. 2006; Korsakov and Hermann 2006; Hermann et al. 2013) consist mostly of aluminosilicate components, appearing as hydrous silicate melts. This last case, however, applies to very deep subduction, probably not directly reflecting on arc magma generation.

Enhanced silicate solubility approaching critical “mixing” of silicate-aqueous fluids is due to solute structure change from (hydrated) ions to monomers and higher polymers (Newton and Manning 2002; 2003; Hunt and Manning 2012). Silica polymerization was recognized in aqueous fluids by in-situ spectroscopic studies both from experiments at high
pressures (Zotov and Keppler 2002), and in FI in UHP metamorphic rocks (Fig. 13; Lago di Cignana metasediments). Although polymerized aqueous fluids can reach a state of hydration which is similar to that in hydrous silicate melts, their physical properties are different, perhaps more akin to that of colloidal silica (e.g., Iler 1979; Hunt and Manning 2012). In the albite-H$_2$O system (Fig. 14), UHP fluids containing up to about 60 wt. % solutes show considerably lower viscosities than hydrous melts, and form a linear trend towards pure water values (Hack and Thompson 2011). Higher polymeric complexes, with characteristics similar to hydrous melts, only form at much greater solute concentrations (well above 80 wt. %; Hack and Thompson 2011).

Based on these observations, it appears not convenient to distinguish UHP aqueous fluid phases in terms of various categories based on the solute (e.g., SiO$_2$) load (e.g., supercritical fluids or supercritical melts). Across the $P$-$T$ range of most subduction zones, silicate solubility can increase multifold in polymerized fluids, as well as the amount of carbonate and sulfide/sulfate complexes, resulting in variable fluid densities and viscosities. Polymerization at high pressure softens the transition from sub-solidus to super-solidus conditions that governs the volatile behavior at shallower crustal conditions. These properties directly reflect on the rate of mass transfer into the mantle wedge, and suggest that deep aqueous fluids can represent effective metasomatic agents in the mantle wedge.

Element recycling by deep subduction fluids

Trace elements

To what extent the physico-chemical properties of UHP fluids, in particular ligand species and concentration, influence elements fractionation between aqueous fluids and matrix rocks during deep subduction directly reflects on metasomatism of the mantle wedge.
Element transfer by solute-poor aqueous fluids at depths of less than 90 km is generally considered very limited, and gives way to transfer via hydrous melts or polymerized aqueous fluids at sub-arc depths (see e.g., Manning 2004; Kawamoto 2006; Spandler et al. 2007; Hermann and Spandler 2008; and references cited). At depths greater than about 90 km, sedimentary, and oceanic rocks in the slab are expected to have different amounts of the same minerals, and at $T$ of about 750-800°C, they would initiate melting if water-saturated (Schmidt et al. 2004). According to several authors (e.g., Johnson and Plank 1999; Rudnick et al. 2000; Hermann and Rubatto 2009), incipient hydrous melting of slab rocks represents the most important source of incompatible elements into the overlying mantle wedge. The LILE-enriched, HFSE (Ti, Zr, Hf, Nb, Ta) depleted incompatible element pattern of arc-magma would result from dissolution of mineral phases, such as phengite (LILE, and Be; e.g., Schmidt and Poli 1998, 2003; Hermann et al. 2006; Hermann and Spandler 2008), epidote (REE, Sr, Th, Pb; e.g., Schmidt and Poli 1998, 2003; Hermann 2002a; Hermann et al. 2006), lawsonite (REE, Sr, Pb, Th, U; e.g., Martin et al. 2011), allanite/monazite (La, Ce, Th; e.g., Hermann 2002b; Hermann and Rubatto 2009), leaving in the residue refractory zircon (Zr, Hf), and rutile (Ti, Nb, Ta).

Kessel et al. (2005b) investigated the fluid/rock and melt/rock partition coefficients of trace elements for water-saturated K-free synthetic basaltic systems from 4 to 6 GPa and from 700°C to 1200°C. Their experimental data suggested that trace element fractionation resembles subduction patterns in arc magmas, showing enrichments in LREE, LILE, Th, U, and Pb, and depletion in HFSE. Differences in the partitioning behavior of trace elements diminish with increasing depth and temperature, and at high $P-T$ conditions, the trace element load of aqueous fluids and hydrous melts becomes increasingly alike, and varies continuously with temperature.
Data on the trace element concentrations of natural UHP fluids have been reported only by a small number of examples, mainly because of the difficulties in analyzing MSI. In these studies (Fig. 15), quantitative element concentrations in MSI were obtained by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) in rehomogenized (for the method, see Malaspina et al. 2006), and in unheated inclusions (for the method, see Halter et al. 2002), using Ca and/or Si as internal standards. Malaspina et al. (2006, 2009) reported the first trace element data for MSI in metasomatic garnet meta-orthopyroxenite (P = 4 GPa, T = 750 °C) from the Maowu Complex in the Dabie Shan. UHP fluid trace element patterns show fractionations similar to arc magmas, with LILE (Cs, Pb, Rb, Sr, Ba), LREE, U, Pb, Th (high U/Th) enrichments, and HFSE (Ti, Zr, Hf, Nb, Ta) depletion (Fig. 15a). They suggested that metasomatic fluids leading to important orthopyroxene and garnet crystallization in peridotites were solute-rich aqueous fluids derived from surrounding crustal lithologies.

In deeply-subducted crustal rocks, the geochemical signature of UHP fluids was investigated by Ferrando et al. (2009) in the Dora-Maira whiteschists, formed by metasomatic processes during prograde HP evolution. Magnesium-rich aluminosilicate aqueous fluids, released during the growth of peak garnet (about 4 GPa and 750°C), are enriched in trace elements compared to the whiteschists (Fig. 15b), and contain fractionated incompatible trace element patterns with positive spikes for LILE, U, and Pb (up to about 100 to 1000 times the mantle; Fig. 15b), and negative HFSE anomalies (Ti, Zr, Nb, Ta). Although some LILE reach “granitic” melt concentrations, element fractionation in fluids does not strictly reflect either an aqueous fluid (i.e., low Ba/Cs, Rb/Cs), or a silicate melt (low LREE, Sr, and Th enrichment trend). Measured LILE enrichments, over LREE and HFSE, are in agreement with a main contribution from the breakdown of phlogopite. Most of the released Rb, Ba and Th, however, remain in phengite, which represents the stable mica at peak metamorphic conditions (Fig. 

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Accessory monazite, Mg-dumortierite, zircon, and rutile in matrix whiteschists control the HFSE and LREE rock budget (Fig. 15b).

Geochemical data like those of the two examples discussed above are extremely valuable, since preserve an experimental flavor, reflecting the chemical control imposed by the metamorphic evolution of rocks. There is an interesting parallel between experimentally-derived fluid-mineral partitioning data which predict enhanced incompatible trace element solubility in UHP fluids at, or close to supercritical conditions (Kessel et al. 2005b), and the capacity of natural fluids to selectively extract LILE and LREE during prograde metamorphism (from HP to UHP conditions). In deep subduction fluids, incompatible element upload is enhanced by mineral dissolution, but governed by metamorphic reactions.

Comparison between examples from the literature further allows us to evaluate the extent of LILE/HFSE fractionation by deep slab fluids. Rutile is a common daughter phase in many FI and MSI (Table 1), pointing to mobilization of HFSE in polymerized fluids. Interestingly, relevant TiO₂ concentrations are observed also in dilute UHP aqueous fluids formed at relatively low $T$, provided that they contain alkalis (cf., Table 1). The efficiency of HFSE uptake appears mainly controlled by fluid properties at high $P$, and directly associated with the matrix slab-rock chemical composition. A similar geochemical behavior is different to that proposed for mass transfer by hydrous silicate melts, where the concentration of HFSE has been recognized to be fundamentally a function of the degree of melting (cf., Hermann and Rubatto 2009, and references cited): in other words, it is temperature dependent.

Accessory minerals controlling the HFSE budget of slab-rocks have been experimentally found to be stable up to 850-900 °C.

Thus, alkali aluminosilicate fluids in subduction zones can mobilize and transport HFSE, also at *sub-solidus* thermal conditions. This is in accordance with experimental and thermodynamic research (e.g., Antignano and Manning 2008; Manning et al. 2008; Wilke et
al. 2012; Sanchez-Valle 2013), and with extensive field evidence (e.g., Selverstone et al. 1992; Rubatto and Hermann 2003; Garrido et al. 2005; Gao et al. 2007). However, HFSE should be lost by UHP fluids during transport into the mantle wedge, before reaching the hotter levels where subduction magmas are generated. According to Garrido et al. (2005) chlorite-bearing peridotites overlying subducting slab could represent the potential HFSE filters removing these elements from slab fluids, without changing their LILE budget. Only after metasomatic re-equilibration, fluids would acquire the LILE-enriched and HFSE-depleted trace element pattern characterizing arc magma.

**Carbon**

A major issue of subduction-zone geochemistry is to model and quantify the fluxes of volatiles released into the mantle wedge, and returned to the exosphere via arc magmatism. Carbon isotopic composition in volcanic gases of arc magmas requires that most of the Earth’s degassed CO$_2$ is recycled (e.g., Alt and Teagle 1999), suggesting that fluids released from the subducting slab metasomatically enrich in carbon the mantle wedge. Modeling the fluxes of carbon ingassing is, however, difficult, since release of carbon during subduction is modeled as a discontinuous process.

In slab rocks, carbon is present in a variety of forms, including carbonate minerals and organic matter, derived from altered oceanic crust and marine sediments. Part of the carbon originally present in crustal lithologies is liberated as CO$_2$, during low-grade metamorphic decarbonation reactions (e.g., Kerrick and Connolly 2001), or fixed as graphite (Foustoukos 2012; Galvez et al. 2013). At greater sub-arc depths, coupled thermal and thermodynamic models strongly suggest that carbonate minerals do not react with silicate phases liberating CO$_2$, and are stable along most subduction geothermal gradients (Connolly 2005; Gorman et al. 2006;
Molina and Poli 2008). In the absence of carbonate melting, most subducted carbon is predicted to be transported deep in the mantle (Dasgupta et al. 2004; Poli et al. 2009).

Fluid inclusions in eclogites-facies rocks have been generally used to support the models, as they contain little to no detectable CO₂, in contrast to fluid inclusions in many other metamorphic environments (e.g., granulites; Touret 2001). Limiting the carbon inventory within FI and MSI to the absence of CO₂, however, can result in an underestimation of the carbon budget in UHP fluids. Carbonates have been reported in FI and MSI from several UHP terranes, often associated with microdiamonds (cf., Table 1; and Dobrzhinetskaya 2012). For example, Dobrzhinetskaya et al. (2007) identified H₂O molecules and carbonate ions in nanometric MSI in Erzgebirge diamonds; Korsakov and Hermann (2006) described carbonate-rich MSI in diamond-bearing calc-silicate rocks from Kokchetav massif. Crystallization from supercritical C-O-H fluids represents the current preferred mechanism by most researchers to account for subduction (i.e., metamorphic) diamond formation (cf., Dobrzhinetskaya 2012; and references cited).

Precipitation of diamond from C-O-H fluids containing carbonate ions, among other species, implies that high fO₂ are prevailing in fluid phases (e.g., CCO buffer, Dobrzhinetskaya et al. 2001; de Corte et al. 2002). Yet, most diamond-bearing UHP metamorphic rocks record P-T conditions (4-8 GPa, and 950-1000°C) that greatly exceed those of arc magma genesis, and hence involve transport of carbon that cannot follow a simple return trajectory to the surface through arc magmatism.

Spectroscopic study of carbon speciation in FI from oceanic-crust metasediments from Lago di Cignana in western Alps shed light on the mechanisms of carbon liberation and transport by deep subduction fluids at P-T conditions directly relevant to slab-mantle-arc transfer (P ≥ 3.2 GPa; T = 600°C). Raman analyses of C species in aqueous FI formed about 100 km depth, revealed appreciable amounts of oxidized carbon dissolved as CO₃²⁻(aq) and HCO₃⁻(aq), along with hydrous and hydrated carbonates and diamond, and no detectable CO₂ (Fig. 13b; Frezzotti ...
et al. 2011; 2014). These results strongly suggest that dissolution of carbonate minerals in aqueous fluids as carbonate ions, in addition or alternatively to decarbonation, is a relevant process for carbon transfer into the mantle wedge during subduction. Further, FI data indicate a major role of water in the transport of carbon at $P$-$T$ conditions that are directly relevant to slab-mantle-arc transfer, with implications for the Earth’s carbon cycle.

Recent geochemical, experimental, and theoretical research suggest similar trends for the release and transport of oxidized carbon during deep subduction (cf., Manning et al. 2013; and references cited). Ague and Nicolescu (2014) proposed that carbonate dissolution, accompanied by silicate precipitation, represents a relevant mechanism for the release of oxidized carbon from subduction zones, based on carbonate $\delta^{18}$O and $\delta^{13}$C systematics, combined with rock and fluid inclusion studies in metamorphic rocks from the Cycladic complex. By computing the dielectric constant of water at upper mantle $P$-$T$ conditions, Pan et al. (2013) predicted the solubility of carbonate minerals in the subducting lithosphere during dehydration reactions. Similar results were obtained by spectroscopy experiments by Sanchez-Valle et al. (2013), which identified carbonate ions as the dominant C-species in oxidized UHP aqueous fluids at $P$-$T$ conditions (650°C and 4 GPa) similar to those of Lago di Cignana rocks. The results summarized above illustrate that investigations on the deep Earth’s carbon cycle have entered a new phase where observations in natural rock systems, thermodynamic models, and experimental research can be merged. New research modifies the magnitude of carbon fluxes in the mantle in subduction zones, and points to a strong need for a better quantification of the properties of carbon species and minerals at depth.
Present review shows that fluid inclusions (FI and MSI) are almost ubiquitous in eclogite-facies crustal lithologies of both continental and oceanic origin. Their composition appears to be controlled by the progressive devolatilization reactions occurring in rocks at HP and UHP conditions, thus preserving a firsthand information on deep subduction fluids.

Water is the dominant volatile species in subduction-zone fluids, which contain variable concentration of solutes, and of other volatiles. At HP conditions down to about 90 km depth (i.e., fore-arc), moderate concentrations of chloride salts, alkalis, Si, and Al, ± non-polar gases are present in aqueous solutions, with properties similar to crustal fluids (e.g., halide ligands); at greater mantle depths (i.e., sub-arc), water-rich phases contain gradually increasing amounts of (alkali) aluminosilicate components (e.g., Si, Al, Ca, Fe, alkalis, Ti, Zr, (SO4)2-, (CO3)2-, and Cl-). Inclusion fluids record the solute structure change from (hydrated) ions to monomers and higher polymers in aqueous fluids at increasing pressure during subduction.

Semi-quantitative chemical data on major and trace element enrichments in FI and MSI, together with experimental and thermodynamic research, unambiguously attest for relevant and selective element mobilization in UHP aqueous fluids, enhanced by mineral dissolution, and ruled by the composition of matrix rocks. Increased element solubility and transport by the aqueous phase is related to silica polymerization, as the pressure and temperature conditions approach the critical endpoint.

It must be emphasized that research on fluid inclusions suggests that deep subduction fluids have more complex chemical compositions than those of model fluids considered by experiments. The finding of substantial amounts of dissolved oxidized carbon in aqueous fluids at sub-arc depths implies a reconsideration of the petrological models supporting liberation of C
into the mantle wedge by metamorphic decarbonation reactions only, and to consider dissolution
and transport of carbon by aqueous fluids a relevant process in deep subduction zones.

Despite the amount of data so far obtained, open questions do remain. The chemical
behavior of other ligands, such as sulfur, is still very poorly constrained, although it is generally
acknowledged that slab-fluid transfer into the mantle wedge causes both oxidation and S
addition. Fluid inclusions could probably provide a most robust insight to the behavior of sulfur
species, by combining chemical and structural analyses. Analytical work should be undertaken to
reveal if the high solute load observed in some inclusions (for example MSI) is a primary
feature, or alternatively results in part from passive dehydration trends. A better quantification of
inclusions post-trapping chemical modifications, including element diffusion, and exchanges
with the host mineral, is also essential.

We believe that fluid inclusion research in subduction zones will provide exciting new
results in the coming years. Although hampered by many analytical difficulties, the study of
fluids in rocks provides the added value of revealing the continuity existing behind the apparent
extreme variations of the physico-chemical properties of aqueous fluids progressively released
during deep subduction.

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CAPTIONS TO FIGURES

Figure 1: Photomicrographs of primary fluid inclusions (FI) in eclogite-facies HP-UHP rocks. (a) Aqueo-carbonic FI elongated parallel to the c-axis of the host OH-rich topaz. Liquid and gaseous CO₂ corresponds to about 30 % of the inclusion total volume. The two
solids are a chloride (s) and gypsum. OH-rich topaz – kyanite quartzite from Sulu, China
(sample RPC546, Plane Polarised Light, PPL). Modified from Frezzotti et al. (2007). (b)

Diamond-bearing aqueous FI in garnet [liquid (L) + vapor (V) > 60% of the total volume of
the inclusions]. Garnetite nodules from Lago di Cignana, Italian western Alps (sample C2BA,
PPL). (c) Chloride-bearing aqueous FI in epidote. L + V represent about 80% of the inclusion
total volume. Two isotropic salts (s) are also present. Phengite-kyanite-epidote eclogite from
Sulu, China (sample RPC778, PPL). Modified from Ferrando et al. (2005a). (d) Chloride-

bearing aqueous FIs elongated parallel to the c-axis of the host kyanite. L+V represent about
40% of the inclusion total volume. Paragonite and ellenbergerite are the solid phases. Pyrope
whiteschists from Dora-Maira, Italian western Alps (sample DM1598, PPL). Modified from
Ferrando et al. (2009).

Figure 2: Photomicrographs of preserved primary multiphase solid inclusions (MSI).

(a) MSI in kyanite showing negative crystal shape. It contains the typical association of
paragonite + muscovite + anhydrite + “alunite”-type sulfate + pyrite + small volume of an
aqueous fluid. OH-rich topaz – kyanite quartzite from Sulu, China (sample RPC547, PPL). (b)

MSI in garnet showing negative crystal shape. They are filled by paragonite + phlogopite +
diamond + quartz + apatite + rutile without apparent fluid. Garnet gneiss, Saxonian

Erzgebirge (sample RAR10, PPL). (c) Back-scattered electron (BSE) image of a freshly-
broken surface of a pyrope including a MSI. Note the preferred orientation of Mg-chlorite and
Na-K-phlogopite. Pyrope whiteschists from Dora-Maira, Italian western Alps (sample
DM69). Modified from Ferrando et al. (2009). (d) MSI in garnet showing negative crystal
shape. In this case, the oriented intergrowth described in Fig. 2c is recognizable also under the
microscope. Pyrope whiteschists from Dora-Maira, Italian western Alps (sample DM1035)

Figure 3: Photomicrographs (PPL: a, d; crossed polarizer: b, e) and back-scattered
images (c, f) of two preserved primary MSI in pyrope from a Dora-Maira whiteschist. Both
MSI have negative crystal shapes and are filled by of Mg-chlorite, Na-K-phlogopite, apatite and pyrite showing periodic crystallization, without any visible fluid phase. Pyrope whiteschists from Dora-Maira, Italian western Alps (a, b, and c: MSI in sample DM1035; d, e, and f: MSI in sample DM1042). Modified from Frezzotti and Ferrando (2007).

Figure 4: Photomicrographs (PPL) of a primary melt inclusion in quartz from Mt. Genis granite (Sardinia, Italy). (a) At magmatic conditions (900°C), the inclusion consists of immiscible silicate-melt and hypersaline fluid. (b) At 20°C, the melt phase is crystallized in a fine-grained aggregate of randomly oriented anhedral to subhedral crystals, coexisting with chlorides, and liquid H2O. Modified from Frezzotti (2001).

Figure 5: Photomicrographs showing petrographic features of MSI. (a) Primary MSI in kyanite. Inclusions have the same dimensions and are oriented along the c axis of the host mineral. OH-rich topaz – kyanite quartzite from Sulu, China (sample RPC 547, PPL). Modified from Frezzotti and Ferrando (2007). (b) Distribution of primary MSI marking the growth zones of the host garnet. Pyrope whiteschists from Dora-Maira, Italian western Alps (sample DM1616, PPL). (c) BSE image of a MSI in pyrope, containing a large incidentally-trapped rutile. Pyrope whiteschists from Dora-Maira, Italian western Alps (sample DM69). Modified from Ferrando et al. (2009).

Figure 6: Collages of BSE images of MSI on an EMP Ca-distribution map of the host garnet (courtesy of B. Stöckhert), showing abundance and the primary distribution of the MSI. The MSI are filled by silicates (quartz + white micas, locally retrogressed) + apatite + rutile ± diamond/graphite. Some inclusions still preserve a negative crystal shape. Other inclusions show reentrant angles at grain edges between inclusion minerals and host garnet and development of offshoots from the corners. Other inclusions show a star-shaped contour with short and thin microfractures lining from the corners. The distribution of the inclusion
types is not systematic. Quartzofeldspathic rock, Saxonian Erzgebirge (modified from Stöckhert et al. 2009).

Figure 7: Outline of the most important post-trapping modifications that can occur in a MSI during exhumation. Stage 1: Fluid trapping. Stage 2: Periodic crystallization of daughter minerals and dissolution and precipitation of the host mineral on the inclusion walls. Stage 3: Early decrepitation event, occurring at the UHP-HP transition, that can induce i) formation of short and large fractures (offshoots) departing from the inclusion corners, ii) crystallization of step-daughter minerals and partial re-crystallization of the host mineral producing irregular contours and re-entrant angles in the MSI, and/or iii) diffusion of water into the host mineral (see, Fig. 10). Stage 4: Daughter mineral crystallization leaves a residual fluid that may produce retrograde metamorphic reactions inside MSI. Stage 5: Late decrepitation event at LP, characterized by the formation of microfractures containing trails of small fluid inclusions, haloes of small fluid inclusions distributed around the inclusion, and/or star-shaped contours in MSI. The BSE image shows a MSI that experienced most of the described post-trapping modifications (see, Fig. 8a, and its caption).

Figure 8: Photomicrographs showing post-trapping modifications in MSI. (a) BSE image of a decrepitated MSI in kyanite, showing minerals and cavities (black). The inclusion is characterized by the typical oriented association of daughter-minerals. Post-crystallization hydration reactions occurred on corundum to form diaspore. Decrepitation features (offshoots and microfractures) are also recognizable. OH-rich topaz – kyanite quartzite from Sulu, China (sample RPC 547). Modified from Ferrando et al. (2005b). (b) Fan-shaped chemical re-equilibration of the host garnet around a MSI. Pyrope whiteschists from Dora-Maira, Italian western Alps (sample DM14, PPL). PPL (c) and BSE (d) images of a MSI in garnet that experienced different post-trapping modifications. A non-equilibrium growth of the host mineral on the inclusion wall produced irregular and re-entrant contours. Subsequent
decrepitation produced microfractures lining from the corners and loss of fluid (FI) and Ca-enrichment in the host garnet. Ky-Phe-Ep eclogite from Sulu, China (sample RPC 778). Modified from Ferrando et al. (2005b). (e) MSI with irregular contours due to a non-equilibrium growth of the host mineral on the inclusion wall. Offshoots due to partial decrepitation are also present (thick arrows). OH-rich topaz – kyanite quartzite from Sulu, China (sample RPC547, PPL). (f) Aqueo-carbonic fluid inclusion in quartz. Irregular contours and reentrant angles are produced by the non-equilibrium growth of the host mineral on the inclusion wall. Alpine quartz vein (sample AV3, PPL).

Figure 9: Photomicrographs showing post-trapping modifications in FI and MSI. (a) Haloes of very small fluid inclusions distributed around single decrepitated MSI within pyrope. Note the irregular habit and the presence of some offshoots from the corners (thick arrows). Pyrope whiteschists from Dora-Maira, Italian western Alps (sample DM1598. PPL). Modified from Frezzotti and Ferrando (2007); (b) Typical example of post-trapping modifications in fluid inclusions from mantle clinopyroxene. The presence of offshoots (thick arrows) and of haloes of very small fluid inclusions is evident. Mantle xenolith from Mt. Iblei (Italy, PPL). (c) Post-entrapment re-equilibrations of a MSI in garnet. The large fracture forms a sort of offshoot and a halo of tiny fluid inclusions is also present. UHP eclogite from Western Gneiss Region (sample V2297, PPL). (d) Primary decrepitated MSI in pyrope showing irregular, star-shaped, contours. Both offshoots (thick arrows) and thin microfractures (thin arrows) are present. Pyrope whiteschists from Dora-Maira, Italian western Alps (sample DM69, PPL). (e) Decrepitated diamond-rich MSI in garnet. Thin microfractures (thin arrows) line from the star-shaped habit. Garnet gneiss, Saxonian Erzgebirge (sample RAR11, PPL). (f) Post-entrapment modification in silicate-melt inclusions in a quartz phenocrysts. The inclusions have thin microfractures (colorless arrows) lining from the inclusion apexes. Swarms of tiny fluid inclusions mantle the microfractures.

Figure 10: Synchrotron FT-IR maps revealing the distribution and the concentrations of water in a Dora-Maira pyrope including some primary MSI (sample DM14). (a) Mapped garnet area (PPL). (b) Qualitative distribution map of liquid H2O within MSI inclusions, revealed by absorption bands in the 3000–3500 cm⁻¹ region. (c) Qualitative distribution map of OH⁻ (bands in the 3500–3800 cm⁻¹ region), showing the hydrogen diffusion from the inclusions into the garnet. (d) Absorbance FT-IR map in the 3000–3800 cm⁻¹ region and relative calculated water contents in garnet (ppm). (e) FT-IR spectrum showing the absorption bands for molecular H2O, and for OH⁻.

Figure 11: P–T diagram showing metamorphic evolution of UHP units discussed in the text. P–T path for the Lago di Cignana Unit is simplified from Groppo et al. (2009). P–T path for the Dora-Maria (Brossasco-Isasca Unit) is inferred combining data from different lithologies (whiteschist, marble, eclogite, calc-silicate rocks: Rubatto and Hermann 2001; Hermann 2003; Castelli et al. 2007; Ferrando et al. 2009). P–T path for quartzite and eclogite from South Sulu is simplified from Ferrando et al. (2005a) and Frezzotti et al. (2007). P–T path for the high-T (dashed line) UHP zones of Dabie-Sulu is simplified from Zheng et al. (2011). The colored squares on the P–T paths represent the trapping conditions of the fluid inclusions reported in Table 1. The compilation of melting reactions in mafic rocks (thick gray lines) and pelites (dashed gray lines) is revised after Schmidt and Poli (2003) and Zheng et al. (2011). The gray-shaded zones representing the solidi for H2O-saturated crustal rocks and the phengite dehydration melting are from Bebout (2007; 2013). Mineral abbreviation after Whitney and Evans (2010) and Kretz (1983).

Figure 12: P–T diagram, modified from Hack and Thompson (2011), showing the silica solubility isopleths (in wt. % SiO₂) in the H2O-SiO₂ system, the prograde subduction-
zone gradients of 5°C/km (cold subduction) and 10°C/km (typical subduction), and the P-T paths of metamorphic rocks in Fig. 11. C is the upper critical endpoint for the H2O-SiO2 system.

Fig. 13: Raman spectra from aqueous fluid inclusions associated with diamonds from Lago di Cignana metasediments. Modified from Frezzotti et al. (2011). a) Silica in solution within a fluid inclusion. The 773 cm\(^{-1}\) peak corresponds to the Si–O symmetric stretch of the Si(OH)\(_4\) monomer, and the peak at 1,017 cm\(^{-1}\) to the deprotonated monomers (SiO(OH)\(_3^{-}\), SiO\(_2(OH)2^{2-}\), and so on). The aqueous fluid also contains SO\(_4^{2-}\), with Mg-calcite (MgCc) and quartz (Qtz). b) HCO\(_3^{-}\), and CO\(_3^{2-}\) in solution within a fluid inclusion, containing Qtz. Asterisks indicate host-garnet Raman bands.

Fig. 14: Plot of viscosity data in the NaAlSi\(_3\)O\(_8\) + H\(_2\)O system: measured values are compared with those obtained from models for fluid and melt (modified from Hack and Thompson 2011).

Fig. 15: In-situ LA-ICP-MS analyses on multiphase solid inclusions. Normalizing values to the primordial mantle after McDonough and Sun (1995). (a) Trace-element concentrations in inclusions + host garnet compared with those in host garnet from mantle wedge garnet peridotites from Sulu (modified from Malaspina et al 2009; courtesy of N. Malaspina). (b) Trace-element concentrations in inclusions + host peak pyrope compared with those in host peak pyrope from continental UHP whiteschists from Dora-Maira. The trace-element patterns of the hosting metagranite, and of peak phengite, and prograde ellenbergerite and dumortierite are also reported. Modified from Ferrando et al. (2009).
Table 1. Collection of published data on deep fluid inclusions

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<th>Metamorphic Belt</th>
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</table>

Continental crust

| Western Gneiss Region | eclogite | 1.5-1.7 GPa 650°C | peak | Hf, Om, and Grt | multi-phase brine fluid inclusions | amphibole, spinel, K-feldspar, quartz | albite, calcite | garnet, Fe-Mg carbonates, Mg-phosphate, Fe-opaques | pyrite, Fe-chlorite | halite | Pb-Bi-Cl | Na-K, Ca-brines with P, Br, F, I, Li, SO$_2$ |
| Dora-Maira | Pre-mylonite | 4.0-4.3 GPa 730°C | peak | Hf, LiH, Grt | fluid inclusions | albite, Mg-chlorite, Mg-phosphate, pyrite | pyrite, Fe-chlorite | halite | chloride |
| Rhodope | Grt-Ky-Bt gneiss | ca 4.5 GPa 1000°C | peak | Lh, Grt | multi-phase fluid inclusions | muscovite, quartz | Mg-oxide, calcite | rhodochrosite | graphite |

| Rhodope | Grt-Ky-Bt gneiss | ca 4.5 GPa 1000°C | peak | Lh, Grt | multi-phase fluid inclusions | biotite, muscovite | quartz | kyanite | graphite |

All the inclusions considered in this work were trapped at UHP conditions or at the HP-UHP or HP-HP transition.


Philpott & Selverstone (1991), Angiboust et al. (2012), Feuz et al. (2011), Groppo et al. (2009), Selverstone et al. (1992), Muller et al. (2009), Fu et al. (2002), Svensen et al. (1999), Svensen et al. (2001), Philpott (1993), Philpott et al. (1995), Castelli et al. (2007), Ferrando et al. (2009), Mposkos et al. (2009), Tso Morari, Window, Dora-Maira conditions.

36) all the inclusions considered in this work were trapped at UHP conditions or at the HP-UHP or HP-HP transition
37) mineral abbreviations after Kretz (1983) and Whitney & Evans (2010)
38) Philpott & Selverstone (1991), Angiboust et al. (2012), Feuz et al. (2011), Groppo et al. (2009), Selverstone et al. (1992), Muller et al. (2009), Fu et al. (2002), Svensen et al. (1999), Svensen et al. (2001), Philpott (1993), Philpott et al. (1995), Castelli et al. (2007), Ferrando et al. (2009), Mposkos et al. (2009), Dora-Maira conditions.

Oceanic crust

| Dora-Maira | Pre-mylonite | 4.0-4.3 GPa 730°C | peak | Lh, Grt | multi-phase fluid inclusions | muscovite, quartz | Mg-oxide, calcite | rhodochrosite | graphite |
| Rhodope | Grt-Ky-Bt gneiss | ca 4.5 GPa 1000°C | peak | Lh, Grt | multi-phase fluid inclusions | biotite, muscovite | quartz | kyanite | graphite |

All the inclusions considered in this work were trapped at UHP conditions or at the HP-UHP or HP-HP transition.


Philpott & Selverstone (1991), Angiboust et al. (2012), Feuz et al. (2011), Groppo et al. (2009), Selverstone et al. (1992), Muller et al. (2009), Fu et al. (2002), Svensen et al. (1999), Svensen et al. (2001), Philpott (1993), Philpott et al. (1995), Castelli et al. (2007), Ferrando et al. (2009), Mposkos et al. (2009), Dora-Maira conditions.

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(a) all the inclusions considered in this work were trapped at UHP conditions or at the HP-UHP or UHP-HP transition
(b) mineral abbreviations after Kinternet (1983) and Whitney & Evans (2010)
(c) Hwang et al. (2001), Dobrohotovskaya et al. (2012), Stichler et al. (2009), Stichler et al. (2001), Stichler et al. (2003), Stichler et al. (2003), Stichler et al. (2006), Stichler et al. (2009)
(d) Dobrohotovskaya et al. (2003), Hwang et al. (2006), Dobrohotovskaya et al. (2003), Konakov and Hermann (2006)
(e) Hwang et al. (2003), Die Corte et al. (1998), Hwang et al. (2004), Hwang et al. (2005)
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**Table 1 continue**

| Metamorphic Belt | Lithology | Peak P-T conditions | Trappping conditions | Host mineral | Name of the inclusions | silicates (Hydrous) | silicates | carbonates | sulphates | sulphides | phosphates | oxides | chlorides | C phases | glass | water | gas | empty cavities |
|------------------|-----------|---------------------|---------------------|-------------|----------------------|------------------|-----------|-----------|-----------|-----------|-----------|----------|--------|---------|---------|------|-------|------|-----------------|
| Betic Cordillera | Opx in eclogite | 1.5 - 2.2 GPa 640 - 750°C | peak | HP Grt | fluid + mineral inclusions | chlorite | olivine | n/a | C-spinel | pyrope | y phase | yes | n/a | n/a | n/a |
| Western | Grt websterite | 3.9 - 4.3 GPa 860-900°C | peak | UHP Sph, Opx and Grt | multi-phase solid inclusions | phlogopite | zircon | kalsilite | orthopyroxene | magnesite | Ba,Cao,CO3 | dolomite | Fe-Ni | sulphide | Ba-sulphide | C-spinel | pyrope | yes | diamond |
| Greats Region | Gt websterite | 5.5 GPa 800°C | peak | UHP Grt | polycrystalline | amphibole | chlorine | Y-phosphate | Fe-Po | sulphides | apatite | monazite | yes | n/a | n/a | n/a |
| ALCAPA Zone | Py-Ap-bearing Sph-Grt peridotite | 2.3 - 3.5 GPa 1030-1050°C | peak | UHP Cr-Sp1 | polyphase solid inclusions | phlogopite | chlorite | Mg-OH | hornblendite | talc | clinohumite | jadeite | us-oxide | U-Th | graphite | carbonatite melt or supercritical fluid |
| Eastern | Gt pyrope | 2.0 GPa 680-880°C | prograde | UHP Grt | high-salinity aqueous inclusions | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
| Dabie-Sulu | Ol-Ap-bearing and Grt-websterite | 3.9 - 4.1 GPa 700 - 800°C | peak | UHP Grt | polycrystalline | amphibole | chlorite | talc | amorphite | amphibole | chlorite | talc | n/a | sulphide | apatite | spinel | solute-rich aqueous fluids |
| Gt peridotite | 4.2 GPa | peak | UHP Grt | polycrystalline | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a | pyrite | spinel | solute-rich aqueous fluids |

**Notes:**
- All the inclusions considered in this work were trapped at UHP conditions or at the HP-UHP or UHP-HP transition.
- Xu et al. (2006), Zhang et al. (2000), Xiao et al. (2008), Shen et al. (2009), Fu et al. (2006).
- Carswell and van Roermund (2005).
- van Roermund et al. (2002), Malaspina et al. (2010), Xu et al. (2008), Xu et al. (2009), Naemura et al. (2009).
- Malaspina et al. (2006), Malaspina et al. (2009).
1. 

2. \( \Delta P > 0 \)

3. offshoots

4. \( \Delta P > 0 \)

5. microfractures with trails and clusters of fluid inclusions

HP -> UHP

Temperature