Fluids at extreme P-T metamorphic conditions:
the message from high-grade rocks

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ABSTRACT. — The study of fluid inclusions in rocks which experienced extreme P-T metamorphic conditions can provide valuable information on the composition of peak fluids, to some extent on their origin, and on fluid-rock interactions which take place in the lithosphere. A review is given, on the basis of the authors' experience, of the major results obtained by fluid inclusions studies in the fields of high pressure and ultrahigh pressure metamorphic rocks (eclogites), high temperature and ultrahigh temperature metamorphic rocks (migmatites and granulites), and high temperature and pressures mantle rocks.

RIASSUNTO. — Lo studio delle inclusioni fluide nelle rocce che hanno subito una evoluzione metamorfica in condizioni estreme di pressione e temperatura permette sia di caratterizzare le fasi fluide presenti alle condizioni di picco, incluse alcune indicazioni sulla loro origine, che di tracciare i processi di interazione roccia-fluido che avvengono nella litosfera. Nel presente articolo sono riportati in forma sintetica i principali risultati ottenuti dallo studio delle inclusioni fluide nelle rocce metamorfiche di alta e ultra alta pressione (eclogiti) e di alta ed ultra alta temperatura (migmatiti e granuliti), e nelle rocce di alta temperatura e pressione del mantello (peridotiti).

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INTRODUCTION

High-grade metamorphic rocks evolve over a large range of pressure-temperature conditions and terrestrial environments: deep subduction settings, upper mantle and lower continental crust. The role of fluid phases attending metamorphism under these extreme pressures and temperatures presently attracts the interest of many earth scientists since these fluid phases: (i) determine mass transfer from subducting plates to the overlying mantle, (ii) percolate and metasomatize vast regions of the upper mantle, (iii) facilitate melt production in the earth's crust and mantle. For this reasons, the study of fluid inclusions in high-grade rocks has experienced a very fast development in the last decade (e.g. - Touret, 2001, Andersen and Neumann, 2001, Scambelluri and Philippot, 2001; Touret and Frezzotti, 2003) substantially improving our understanding of petrologic processes, particularly about the role of fluid phases at crucial geodynamic environments.

A major result arising from fluid inclusion studies is that deep and hot rocks show striking differences in the nature and abundance of fluid inclusion populations: abundant in many high-T rocks, rare in most high-P rocks, gaseous-dominated (CO_2) in migmatites and granulites, aqueous dominated in eclogites, melt-dominated (silicate and/or carbonate) in mantle rocks (Touret and Frezzotti, 2003). Despite such a variability, all fluid inclusion studies significantly contribute, through the reconnaissance of successive generations of inclusions, to relate the conditions of fluid trapping with the P-T history of the host rocks and minerals, as well as to an understanding of fluid/melt/rock interactions in the deep crust and lithosphere.

The degree of preservation of inclusions formed at high P-T conditions, in fact, is not related to the absolute values of P and/or T experienced by the host rock (Fig. 1). Within a given host mineral, inclusions often behave as closed volumes, in which pressure and temperature are not independent variables. Both are related by the equation of state of the enclosed fluid, resulting in a linear relation (isochore) in P-T space. Thus, if deep rocks come to the surface along a trajectory (P-T path) which remains parallel to the fluid isochore, then internal (fluid) and external (rock) pressures will be equal at any reference temperature (Touret, 2001). This fundamental rule (*isochoric behavior*, Touret, 1992) explains why high-grade metamorphic rocks may preserve more - at times many more - fluid inclusions, than shallower protoliths (e.g. low-grade metamorphic and low-pressure magmatic rocks).

The focus of this paper is to review some major recent literature on fluid inclusions in deep and hot metamorphic rocks. This involves both a consideration of the general properties of fluid inclusions in rocks which experienced a different evolution, and an emphasis on what these data can tell us about fluid-rock interaction and fluid evolution processes. Discussed examples concentrate on fluid inclusions formed in the most extreme P-T
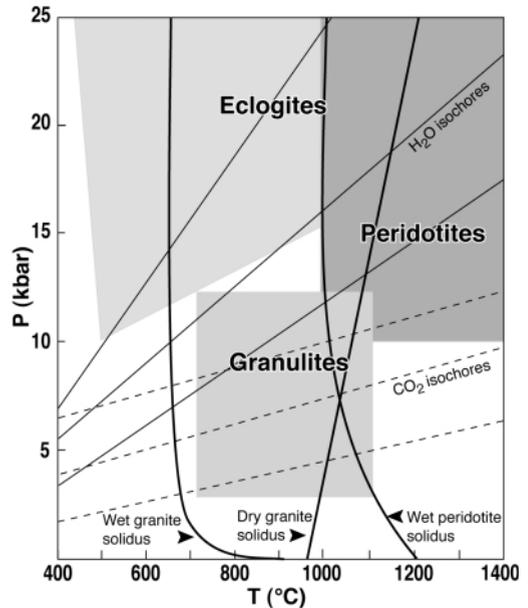

Fig. 1 – P-T representation of HP-HT metamorphic rocks (eclogites, migmatites/granulites, and peridotites). P-T stability fields of the different rock types are compared with isochores for aqueous and carbonic fluids: aqueous inclusions will be better preserved in eclogites, while carbonic inclusions in granulites.

conditions (Fig. 1): subduction zones (eclogites), crustal melting (migmatites), and mantle processes (mantle metasomatism).

FLUIDS IN HIGH AND ULTRAHIGH PRESSURE ROCKS: STORAGE AND RELEASE OF SALINE AQUEOUS FLUIDS DURING SUBDUCTION

Survival of primary fluid inclusions in eclogite-facies rocks proves the presence of excess fluid during high (HP) and ultrahigh (UHP) pressure metamorphism of most slab components, and enables monitoring the deep fluid/rock interactions. The studies of fluid inclusions in eclogite-facies rocks document that subduction fluids are dominated by saline aqueous solutions with minor N_2 and CO_2 (Andersen *et al.,* 1989; Scambelluri and Philippot, 2001; Touret and Frezzotti, 2003).

These compounds are stored in rocks during their shallow (oceanic) hydration and flux the mantle at subduction zones, thus triggering earthquake and volcanic activity at convergent plate margins.

The main fluid inclusion types recognized in the high and very-high pressure rocks are: (1) variably saline aqueous inclusions, (2) gaseous CO_2-N_2 inclusions, locally associated with the aqueous ones. Group 1 inclusions can be over-saturated, thus displaying salt crystals, and locally precipitate numerous mineral daughters, some of which (e.g. rutile, apatite, zircon, micas) are repositories for incompatible elements (Philippot and Selverstone, 1991; Stoeckert *et al.*, 2001; Scambelluri *et al.*, 1997; 2001). Fluid inclusions in HP rocks are present in various textural occurrences: in minerals from variably deformed rock domains, and in veins. Fluid inclusions in rock-forming minerals are rare. They form core clusters in porphyroblasts, as well as in mineral inclusions armoured by coarse HP crystals, and are interpreted as dehydration fluids released at early stages of devolatilization (Scambelluri and Philippot, 2001). Examples are the low-salinity aqueous inclusions present in relict kyanite from the Alpine Dora-Maira coesite unit (Sharp *et al.,* 1993; Philippot *et al.,* 1995). Primary aqueous inclusions with variable salinities and gas species (N_2, CO_2 and CH_4) in high- ultrahigh-pressure minerals of the Dabie-Sulu terrains (China) likely represent remnants of pre-metamorphic meteoric water modified during subduction metamorphism (Fu *et al.,* 2003).

Early eclogitic fluids are hosted in coarse omphacite (less frequently garnet) of eclogites of the Alps (Monviso, Rocciavrè, Voltri and Mt Emilius; Philippot and Selverstone, 1991; Vallis and Scambelluri, 1996; Scambelluri *et al.,* 1998) and of Californian and Dominican blueschist melanges (Giaramita and Sorensen, 1994). These are tubular aqueous inclusions containing liquid + vapor ± solid with long dimensions parallel to crystallographic faces of omphacite (Fig. 2a). Salinity is generally low, although 17-21 wt% and 32-45 wt% NaCl
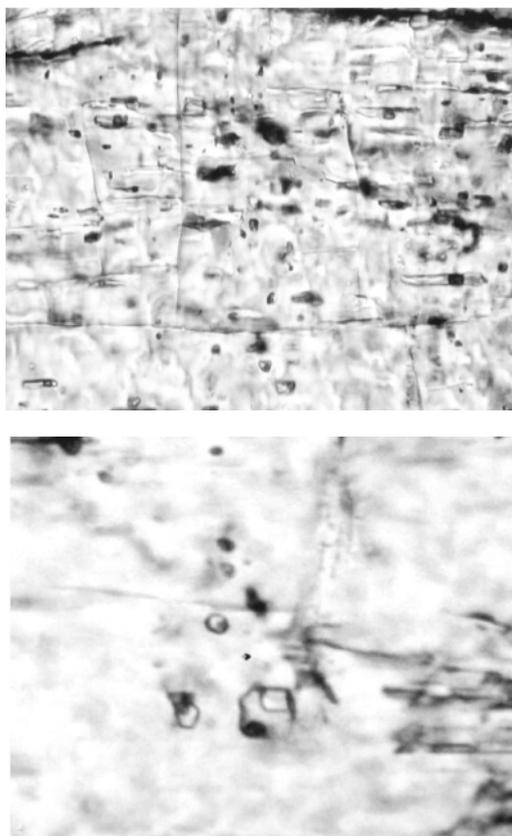

Fig. 2 – Micrographs showing fluid inclusion textures in eclogitic rocks. a) core clusters of fluid inclusions in omphacite porphyroclasts from eclogitic mylonites. b) omphacite fibres from high-pressure veins in eclogites, showing core cluster of primary fluid inclusion liquid + vapour and liquid + vapour + halite inclusions in vein omphacite from eclogites. Average inclusion size is 20 μm.

equivalents were detected in the Monviso and Rocciavrè inclusions. In Norwegian and some Alpine HP rocks, eclogitization of precursor granulites in response to fluid infiltration along shear zones (Austrheim, 1987; Scambelluri *et al.,* 1998) was accompanied by compositional changes of the associated fluids. In Western Norway, early low-salinity $N_2 \pm CO_2$ aqueous inclusions are post-dated by anhydrous CO_2-N_2 fluids, related with advanced stages of eclogitization, and of fluid interaction with

siliceous melts percolating the shear zones (Andersen *et al.,* 1989; 1993). In addition to the anhydrous CO_2-N_2 fluids, water partitioning into percolating melts and/or into hydrous phases during eclogite-facies metamorphism might have caused the formation of highly saline fluid inclusions with up to 18 solid phases documented in omphacite of the Norwegian eclogites (Svensen *et al.,* 1999). In the Austroalpine Mt. Emilius continental unit, fluid-induced eclogitization of granulites, was followed by fluid redistribution in HP veins (Scambelluri *et al.,* 1998). Fluid evolution in such rocks is recorded by entrapment of variably saline inclusions in rock- (10 to 25 wt% NaCl)) and in vein-forming (25 to 50 wt% NaCl) omphacite and garnet. The salinity change from rock to vein fluids reflects water consumption during eclogitic hydration of the precursor granulite, that increased from 2 to 5 times the chloride contents in the residual fluid (Scambelluri *et al.,* 1998).

Fluid inclusions in HP veins are the most widespread in eclogite-facies rocks. In the Alps, HP veins are present in ophiolitic eclogites and serpentinites, as well as in the eclogitized continental crust. Strong similarity in the mineralogy of host rocks and veins, together with the stable C-O-H isotope signature of eclogites, indicate local derivation and short range mobility of the vein fluid (Nadeau *et al.,* 1993; Getty and Selverstone, 1994; FrühGreen *et al.,* 2001). The veins display variable textures and contain: (i) blocky minerals with oscillatory zoning and random orientations; (ii) stretched fibrous crystals. Fluid inclusions occur in both vein types: the growth surfaces of zoned crystals are decorated by primary inclusions and are cut by pseudosecondary trails; the stretched omphacite fibres display clusters of tubular inclusions matching the long axis of fibres (Fig. 2b) (Philippot and Selverstone, 1991; Scambelluri *et al.,* 1997; 1998). The inclusions contain liquid + vapour ± salt cube(s) and correspond to briny aqueous solutions with up to 50 wt% salts; presence of additional solid phases indicates that the fluids carried substantial amounts of major and trace elements dissolved from the surrounding rocks (Philippot and Selverstone, 1991). These highly loaded inclusions were taken as evidence for the presence of aqueous solutions rich in dissolved rock components (supercritical fluids?) during eclogitization (Scambelluri and Philippot, 2001). Comparable conclusions are proposed by Stöckhert at al. (2001) after a detailed study of diamond-bearing solid inclusions in garnets from the Munchberg gneiss complex. These multiphase solid inclusions were likely precipitated for a supercritical C-O-H silicate fluids circulating at ultrahigh-pressure conditions.

The fluid inclusion features presented here shed light on the processes of element recycling in deep subduction environments. Scambelluri *et al.* (1997) and Philippot *et al.* (1998) recognized that the eclogitic fluid inclusions in the subducted oceanic lithosphere contain elements such as Cl, Sr, B, and B originally uptaken at the ocean floor. A number of exogenic components thus become recycled in the subduction fluid. Due to scarce fluid mobility, as documented by the stable isotope imprints of the HP and UHP rocks, such substances remain entrapped in the slab and are re-injected into deeper levels of the upper mantle.

<center>Fluids in high-temperature rocks: fluid and melt inclusions in migmatitic xenoliths from the Neogene Volcanic Province of SE Spain</center>

The high-temperature (HT) and ultra-high-temperature (>900°C, UHT) metamorphic conditions which can be attained under favorable geodynamic conditions in the mid- to lower crust are able to induce the partial melting of fertile protoliths, and the generation of felsic anatectic magmas. Therefore, in migmatites and granulites, where partial melting has likely occurred, the term «fluid» has a wider meaning, and includes both volatile rich phase(s) and silicate-rich melt(s). When

both «fluids» are present in the rock (i.e. magmatic immiscibility), and trapped as inclusions in minerals, the distinction between fluid inclusions s.s. and melt (or glass) inclusions is generally made.

As the presence and composition of the fluid phase strongly affects the behavior of a rock upon melting, the fluid-solid-melt equilibria have been extensively studied. From a theoretical point of view, and only considering melting of a metasedimentary «pelitic» crust, it has been shown that only the initial stages of anatexis generally take place under fluid-present conditions, and that subsequent extensive melting is likely to be attained only by fluid-absent melting (e.g. Thompson 1982; Le Breton and Thompson 1988; Vielzeuf and Holloway 1988). This is valid only in the presence of pure aqueous fluids: when the carbonic component is added to the system, the fluid/melt partitioning behavior of the different C-O-H species needs to be considered (e.g. Cesare and Maineri, 1999). Experimental evidence suggests that H_2O preferentially partitions into the melt, with solubilities depending on P, T and melt composition (e.g. Holtz *et al.,* 2001). Conversely, CO_2 and CH_4 have a very low solubility in granitic melts (e.g. Holloway, 1976; Lowenstern, 2001), and concentrate in the fluid phase or in coexisting solids such as cordierite (e.g. Harley *et al.,* 2002). In natural examples, selective H_2O removal into the melt and concentration of carbonic species in the residual fluid, is the principal mechanism invoked to explain the common occurrence of CO_2-rich inclusions in migmatites and granulites (e.g. Touret, 1971, 2001; Fitzsimons and Mattey, 1994)

One major drawback of fluid inclusion studies in HT migmatites and granulites is that the slow cooling history of these regionally metamorphosed rocks causes crystallization within melt inclusions, recrystallization of host minerals, as well as post-entrapment modifications of fluid inclusions. Therefore, the only possibility (if any) to detect directly coexisting carbonic fluids and melts in HT settings is to investigate rapidly uprisen and quenched crustal xenoliths within volcanic extrusions, where both textures and inclusions had no time to reequilibrate. A unique occurrence is provided by the restitic enclaves and xenoliths of El Joyazo and Mazarron, in the Neogene Volcanic Province (NVP) of SE Spain. These rocks, extensively studied in recent times (Cesare *et al.,* 2003a, and references therein) indeed represent the melanosome of an «erupted migmatite» (Zeck, 1970), and preserve at best the mineralogical, chemical and microstructural signatures of anatectic rocks, as testified by the widespread occurrence of fresh glass in them.

At El Joyazo most enclaves contain the assemblage biotite-garnet-sillimanite-plagioclase-melt-graphite (Cesare *et al.,* 1997; 2003a) which formed at T>850°C, P ≈ 7 kbar.

The crustal enclaves of El Joyazo display two main inclusion occurrences. Most are rich in melt inclusions, but lack fluid inclusions (Cesare and Maineri, 1999): in such cases, primary melt inclusions are trapped (Fig. 3a) in virtually all rock-forming minerals. Melt inclusions are particularly abundant in plagioclase, and their size (up to 80 mm) enables the in-situ analysis of their composition, which corresponds to a felsic peraluminous rhyolite (Cesare *et al.,* 1997, Cesare and Gomez-Pugnaire, 2001). Such a leucogranitic composition is compatible with melt generation by anatexis of a metapelitic protolith at the estimated P-T conditions, the solid phases being the peritectic products. Despite the absence of fluid inclusions in these enclaves, Cesare and Maineri (1999) concluded that the melting process was fluid-present, but that the fluid composition had an $X_O=1/3$ (Connolly and Cesare, 1993), thereby allowing complete partitioning of the H_2O component in the melt, and speciation of the carbonic components to produce graphite and additional H_2O.

A few enclaves from El Joyazo also contain fluid inclusions often associated with melt inclusions with microstructures, which indicate immiscible trapping (Fig. 3b). Although many examples of secondary entrapment have been
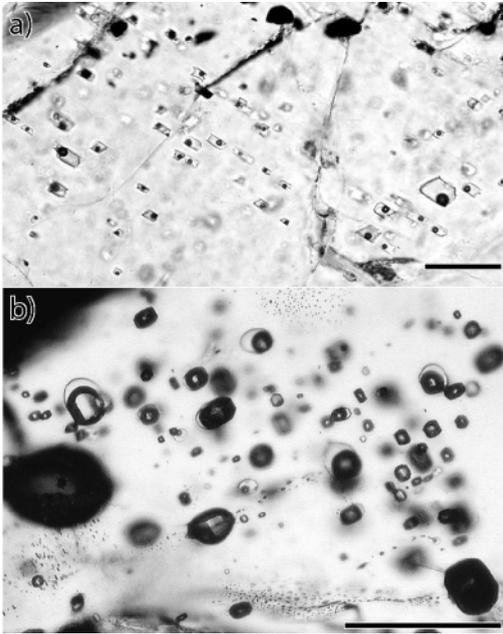
Fig. 3 – a) Silicate melt inclusions in plagioclase from an enclave of El Joyazo. Scale bar = 100 μm. b) Immiscible trapping: coexisting melt (thin border) and fluid inclusions (dark monophase, thick border) in cordierite from an enclave of El Joyazo. Some «mixed» inclusions contain both fluid and melt. Scale bar = 100 μm.

observed, figure 3b provides clear evidence that immiscible fluids were primarily trapped during cordierite and plagioclase growth. The fluid inclusions always contain one phase at ambient T, and often contain daughter crystals of calcite when trapped within plagioclase, similarly to the example studied by Kleinfeld and Bakker (2002). The fluid composition, determined by Raman spectroscopy, is CO_2-dominated, although minor amounts (< 5 mol%) of CH_4, CO and N_2 can be present.

Fluid-melt immiscibility is extensively recorded also in the enclaves of Mazarron. Unlike those of El Joyazo, these restites contain abundant cordierite and andalusite, and testify for lower pressures of equilibration (2-4 kbar), still at HT conditions (800-900°C; Cesare *et al.,* 2003a, b). The microstructures of immiscible trapping are similar to those

observed at El Joyazo, fluid and melt inclusions being again hosted by plagioclase and cordierite. Microthermometry and Raman studies of immiscible fluid inclusions in cordierite show that the fluid is a low-density CO_2-CH_4 mixture, with up to 0.2 X_{CH4}. The glass in the melt inclusions has a corundum-normative felsic rhyolitic composition.

The fluid and melt inclusions in the xenoliths of the NVP of SE Spain are an exceptional example of immiscibility between anatectic leucogranitic melts and CO_2-dominated fluids at mid-crustal conditions. They also allow speculation on the origin of CO_2 in these rocks: if a carbonic component was present in the graphitic metasediments before partial melting, fluid inclusions should be always associated with melt inclusions, but this is not the case for most of the enclaves of El Joyazo. On the other hand, one can observe that carbonic inclusions generally occur in Bt-free or Bt-poor rocks, i.e., in rocks where biotite has melted to form cordierite, ilmenite and/or garnet. Based on such observation, a genetic relationship between biotite melting and CO_2 presence in the rock can be inferred, in support of the model of Hollister (1988) on CO_2 formation by oxydation of graphite during melting of of Fe^{3+}-bearing biotite. This is an additional process to explain the ubiquitous presence of CO_2 in granulites, which often requires the influx of fluids from external sources such as mantle-derived magmas (e.g. Touret and Huizenga, 1999).

SOURCE OF MANTLE (AND POSSIBLY LOWER CRUSTAL) CO_2: THE CARBONATE CONNECTION

Fluid inclusions in most mantle xenoliths contain pure or nearly pure CO_2. However, minor amounts of other volatiles (e.g. H_2O, N_2, CH_4, CO, SO_2, noble gases) in inclusion fluids are reported in few cases (see Andersen and Neumann, 2001). Such exotic components in fluid inclusions provide constraints on the fluid regimes in different parts of the upper mantle,

on the evolution of mantle reservoirs, and give information on the nature of metasomatic processes. Additional fluid components in CO_2 inclusions have been recognized in mantle xenoliths from continental and arc settings (N_2, CH_4, CO; e.g. Bergmann and Dubessy, 1984, Huraiova and Hurai, 1991), and in a few examples from ocean island settings: CO_2-N_2 inclusions are present in spinel dunites from Lanzarote, Canary Islands (Andersen *et al.*, 1995), CO_2-SO_2 inclusions in lherzolites from Tenerife, Canary Islands (Frezzotti *et al.*, 2002b), and CO_2 + unknown low-melting compound(s) inclusions in lherzolites and garnet pyroxenites from Hualalai and Ohau, Hawaii (Murck *et al.,* 1978, Frezzotti *et al.,* 1992). However, the presence of volatile-bearing daughter minerals and glasses of different types associated with the CO_2 inclusions makes it clear that chemically complex fluids are present in the upper mantle also in ocean island settings.

In mantle-derived rocks, the study of melt inclusions is closely linked to the study of fluid inclusions. The association of melt and fluid inclusions may illustrate a remarkable variety of melt-related immiscibility phenomena: silicate-silicate, silicate-sulfides (or other ores), silicate-carbonate, silicate/carbonate-fluids (Roedder, 1984, Frezzotti, 2001). The morphological evidence is always the same: a droplet (globule) of one phase within a matrix of contrasting composition. This direct evidence, however, might be blurred by further evolution of the unmixed melts, such as the epitaxial crystallisation of mineral phases. Among the different types of immiscibility, silicate/silicate, silicate/sulfide- and silicate/fluid have been the subject of many studies*,* with conclusions widely accepted by the majority of scientists (Frezzotti, 2001). This is not the case for immiscibility involving carbonate melts: despite the fact that examples have been recognized in ultramafic xenoliths from the Spitsbergen, the Taha Archipelago, the Canary Islands, and the Kerguelen archipelago (Amundsen, 1987; Ionov *et al.*, 1996; Schiano and Clocchiatti, 1994; Schiano *et al.*, 1992, 1994; Frezzotti *et al.*, 1994, 2002a and b; Kogarko *et al.*, 1995, Mattielli *et al.*, 1999), these remain, however, either ignored, or fiercely discussed in the literature, particularly in melt inclusion studies**.**

Two aspects are significant, in order to explain the rarity of carbonates in mantle rocks: (i) with the exception of carbonatites, which correspond to a very specific (and infrequent) mode of occurrence, carbonate melts are ephemeral (Green and Wallace, 1988; Yaxley *et al.*, 1998): immediately or shortly after their formation, they may be consumed by reactions with mantle wall rocks (Yaxley *et al.*, 1991). (ii) In most cases, carbonates coexisting with silicates do not survive transport, even in the fastest ascending magma, because of rapid decarbonation upon decompression (Canil, 1990).

Central to this debate is the existence of carbonate-rich melts in the upper mantle. In most studies of mantle-derived xenoliths no traces of carbonates are found and interaction of mantle peridotite with carbonate melt has been indirectly inferred from petrographic (i.e. unusual high ratios of clinopyroxene to orthopyroxene; presence of apatite, amphibole, mica) and/or geochemical features (LILE enrichment decoupled from Ti abundance) (Green and Wallace, 1988; Yaxley *et al.*, 1991, 1998; Ionov *et al.,* 1993, 1996; Mattielli *et al.,* 1999).

Rare example of carbonate remnants can be found mostly in inclusions (Amundsen, 1987; Ionov *et al.,* 1996 Schiano *et al.,* 1992, 1994; Kogarko *et al.,* 1995). A number of these occurrences are debatable (e.g. secondary carbonates, not primary melts), but droplets of immiscible carbonates, representing quenched melts, have been observed at La Gomera (Canary Islands). In particular Frezzotti *et al.* (1994, 2002a) describe melt inclusions in Ti-Fe-rich cumulate xenoliths from La Gomera that contain both a silicate glass and a carbonate, showing a successive, double immiscibility (silicate/carbonate and carbonate/CO_2). At first sight, remnants of this former melt, which occur also as late

microveins, could be taken as altered olivine. Data by Frezzotti *et al.* (1994, 2002 a and b), however, suggest metasomatic alteration directly associated to carbonate melts, related to Canary Island volcanism.

The presence of a volatile-bearing, siliceous, alkaline, carbonatite melt in the upper mantle beneath Canary Islands is in excellent agreement with other data. Mantle xenoliths from Tenerife show evidence of Ca-metasomatism with significant addition of highly incompatible trace elements, K and Na, including formation of phlogopite (implying addition of H_2O), leaving the metasomatized rocks very depleted in Al and Ti (Neumann *et al.,* 2002). Neumann *et al.* (2002) propose that this metasomatism was caused by H_2O-bearing, silicic carbonatite fluids. Frezzotti *et al*. (2002b) describe fluid inclusions in harzburgite and lherzolite xenoliths from Tenerife that contain complex inclusions whose chemical components correspond very well with those added through the Ca-metasomatism in the upper mantle beneath Tenerife.

The carbonate-rich melts probably derived from low degrees of partial melting of peridotites at deeper levels. They were able to circulate through a complex system of veins and considerably heated the xenoliths before their entrainment in the host basalts. Carbonate melts are unstable in the P-T stability field of many peridotites, and their preservation could be possible only within the inclusions. This means that a large number of CO_2 fluid inclusions in mantle xenoliths may have formed by breakdown of carbonates. If this hypothesis is true it implies that a large part of the CO_2 present in the mantle may originate via degassing of ephemeral carbonate melts or carbonates.

Concluding remarks

Fluid inclusion studies represent a valuable tool to our understanding of deep fluid evolution. Despite extreme P-T conditions, preserved fluid remnants bring an essential contribution to the knowledge of deep-crustal or mantle fluids. Many problems remain to be elucidated, particularly on the fluid source. Some features are rather clear. For example, micas and feldspar may contain a significant amount of nitrogen in their structure in the form of NH_4^+ ions, which are released when these minerals break down (Andersen *et al.,* 1991). Most N_2 in eclogites is found at the stage where these minerals become unstable and such a link cannot be accidental. Conversely, the origin of CO_2 is highly controversial: along with the mechanisms outlined above, in many cases CO_2 seems to be related to fluid-magma interaction: that is, dissolved in magmas and expelled during progressive magma crystallization (Touret, 1992).

Further efforts are needed to characterize the origin and composition of deep fluids (either gases or melts) in high P-T rocks, by study of fluid inclusions, stable isotopes, thermodynamic modeling from mineral equilibria and experimental simulation. Realization of this goal may eventually allow us to recognize processes in the mantle, including crust-mantle interactions, mantle metasomatism, and recycling of crustal material through subduction.

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