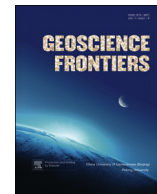
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Research paper

CO₂, carbonate-rich melts, and brines in the mantleMaria-Luce Frezzotti^{a,*}, Jacques L.R. Touret^b^a Department of Earth and Environmental Sciences, University Milano Bicocca, P.zza Della Scienza 4, 20126 Milano, Italy^b Mineralogy, Université Pierre et Marie Curie, 4 Place Jussieu, 75272 Paris Cedex 05, France

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ABSTRACT

This paper reviews the origin and evolution of fluid inclusions in ultramafic xenoliths, providing a framework for interpreting the chemistry of mantle fluids in the different geodynamic settings. Fluid inclusion data show that in the shallow mantle, at depths below about 100 km, the dominant fluid phase is CO₂ ± brines, changing to alkali-, carbonate-rich (silicate) melts at higher pressures. Major solutes in aqueous fluids are chlorides, silica and alkalis (saline brines; 5–50 wt.% NaCl eq.). Fluid inclusions in peridotites record CO₂ fluxing from reacting metasomatic carbonate-rich melts at high pressures, and suggest significant upper-mantle carbon outgassing over time. Mantle-derived CO₂ (±brines) may eventually reach upper-crustal levels, including the atmosphere, independently from, and additionally to magma degassing in active volcanoes.

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1. Introduction

Volatiles (e.g., C, O, H, S, and halogens) in the Earth's upper mantle include accessory phases, nominally anhydrous minerals, along with fluid/melt phases (e.g., Thompson, 1992; Green and Falloon, 1998; Bolfan-Casanova et al., 2000; Wyllie and Ryabchikov, 2000). Fluids and volatile-rich melt phases are important mass-transfer agents, influencing chemical and physical properties of the upper mantle. Knowledge of composition and fluxes of these mobile volatile-rich phases is thus important for understanding lithosphere deformation and recrystallization processes, peridotite metasomatic enrichments and partial melting behavior, and fluxes of volatiles to the exosphere (e.g., Asimow and Langmuir, 2003; Hirth and Kohlstedt, 2003; Katayama and Karato, 2008).

Fluid inclusions in peridotites are natural examples of shallow mantle fluid/melt phases. In 1965, Roedder (1965) discovered 'liquid CO₂' fluid inclusions in olivine within ultramafic xenoliths in 72 alkali basalts occurrences scattered all over the world. In the fluid inclusions, the liquid phase was only evidenced by a coexisting gas bubble. The following remark written in his standard book (Roedder, 1984) is of interest: "As nodules had been studied intensively for many years prior to 1965 without a single report of CO₂ fluid inclusions, some explanation is in order. Most of the fluid inclusions studied appear, at first glance, to be merely opaque specks (i.e., solid inclusions) in the enclosing minerals, and hence are easily overlooked".

Six years after Roedder's discovery, CO₂-rich fluid inclusions were described in granulites by Jacques Touret, firstly in southern Norway (Touret, 1971), then in most granulite occurrences worldwide (Touret, 1977, 1981, 1985). A number of possible fluid sources are possible. These include internal, fluids generated by metamorphic reactions and/or partial melting in the lower crust, or external fluids generated by infiltration from a deep source (e.g., mantle-derived syn-metamorphic intrusive; cf., Touret and Huizenga, 2012a,b). This last possibility concerns especially high-, and ultrahigh-temperature granulites, which require an extremely effective heat supply in order to reach metamorphic temperatures approaching or even exceeding 1000 °C (Kelsey, 2008).

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CO₂-rich fluids are particularly important in mantle processes. Deep CO₂ is found in virtually all examples of continental and oceanic volcanism. Extremely CO₂-enriched volcanic gases, CO₂-rich ground water, and carbonatites are present in rifted areas. In addition, surface gas-geochemical observations suggest the existence of a diffuse 'non-volcanic' (in the sense of Kerrick (2001)), deep CO₂ over large regions, which is being outgassed from the mantle and/or the lower crust to the exosphere through extremely variable geological processes, including metamorphism, mountain building, or extensional geodynamics (Touret, 1992; Frezzotti et al., 2009; Touret and Huizenga, 2012b).

A number of review articles have previously discussed the importance of CO₂-rich fluid inclusions in mantle xenoliths (e.g., Roedder, 1984; Pasteris, 1987; Andersen and Neumann, 2001; Hansteen and Klügel, 2008), which also give details on minor components, mostly sulfide/sulfate and carbonate for the solid phases, and other non-polar fluids than CO₂. Recently, detailed studies have suggested a connection between carbonate-rich melts and CO₂ (±brines) fluid inclusions at upper mantle depths, prior or during the production of eruptive magmas (e.g., Frezzotti et al., 2002a,b, 2010, 2012b; Frezzotti and Peccerillo, 2007; Touret, 2009; Berkesi et al., 2012; Kawamoto et al., 2013). The present review aims at presenting some of the essential issues on natural fluids in the shallow mantle, which illustrates the remarkable similarity between processes leading to volcanism on the one hand, and the relation with mantle metasomatism on the other, as well as degassing in general from the Earth's mantle.

2. Occurrence of mantle CO₂ inferred from fluid inclusion density

CO₂-rich fluid inclusions are extremely abundant within mantle rock-forming minerals. The most straightforward method to obtain the fluid pressure at the time of final closure of the mineral cavity is by micro-thermometric studies. CO₂ densities (fluid inclusion isochore) are readily obtained from the homogenization temperature (Th_L; disappearance of the liquid/vapor interface) measured at room temperature (Touret, 1981; Roedder, 1984). Thousands of micro-thermometric measurements done in fluid inclusions in mantle xenoliths and volcanic lavas worldwide have explored the distribution of CO₂ densities (Andersen and Neumann, 2001; Hansteen and Klügel, 2008, and references cited therein). These studies demonstrated that most fluid densities fit a bimodal distribution, towards low and high values. Fig. 1, modified from Frezzotti and Peccerillo (2004), shows the predicted two groups of fluid inclusions based on density measurements.

(1) Relatively low-density CO₂-rich fluid inclusions (Th_L generally ≥ 20 °C) are by far the most abundant (Fig. 1a). These are present, not only in minerals from mantle xenoliths, but also in lava phenocrysts, typically associated with melt remnants (glass-containing inclusions). They can also occur in partly melted minerals along grain boundaries, quite abundant in many mantle xenoliths, although often ignored. This type of fluid inclusion can occur in any rock-forming mineral (olivine, pyroxene, feldspars), provided that it has reached at least few mm in size (e.g., lava phenocrysts). For a reference temperature of 1200 °C, pressures calculated for this low-density group are generally in the 0.1–0.3 GPa range (Fig. 1), corresponding to a depth generally from about 2 to 7 km (lithostatic pressure regime). Such depths correspond typically to the last episodes of magma rest, prior to the volcanic eruption. The influence of these fluids on the eruption mechanism is shown by the fact that the abundance of these low-density fluid inclusions varies grossly, according to the type of eruption. They are quite rare,

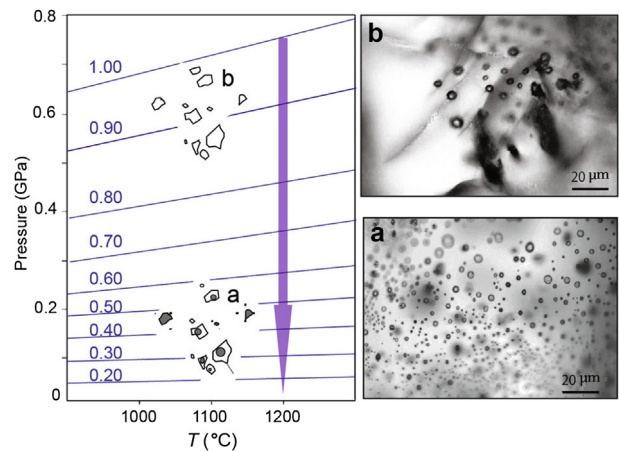


Figure 1. Evolution of CO₂-rich fluid inclusions in mantle xenoliths during decompression. At any depth, pressure in the fluid inclusion is defined by the intersection of a constant reference temperature (1200 °C = T ascending basalt magma; lilac arrow) and the CO₂ isochore (blue solid lines, numbers = CO₂ densities in g/cm³). Two examples of final fluid inclusion equilibration in different settings: (a) shallow magma chamber, P = 0.1–0.2 GPa, the most common case before eruption. Olivine phenocrysts from the Azores basalts, modified after Zanon and Frezzotti (2013); (b) deep magma chamber, P = 0.6–0.7 GPa, presumably close to crust-mantle boundary. Spinel lherzolites of Hawaii, modified after De Vivo et al. (1988).

or even lacking, in quiet lava flows, while quite abundant in explosive volcanic pipes (Bilal and Touret, 1976).

(2) High-density CO₂-rich fluid inclusions are far less abundant (Th_L generally < 0 °C; Fig. 1b). Some fluid inclusions can reach densities in the field of a 'super dense' CO₂ fluid, with homogenization temperatures below the CO₂ triple point (T = –56.6 °C) in the presence of solid CO₂, along the metastable extension of the liquid-vapor curve. Th_{L,s} as low as –70 °C have been measured in peridotites from Hawaii. This minimum is generally not exceeded in mantle rocks, because the metastable domain hardly exceeds 20 °C, from –56.6 to about –70 °C (Frezzotti et al., 1992). The density of CO₂-rich fluid showing this micro-thermometric behavior is 1.21 g/cm³, and corresponds to trapping pressures of about 1.8–2 GPa at 1200 °C.

Fluid density data can be problematical due to fluid inclusion post-trapping effects. Lithostatic pressures derived from CO₂ fluid isochores are in all cases considered to be minimum values (cf., Andersen and Neumann, 2001; Touret, 2001), determined by the strength of the mineral host (e.g., olivine; Wanamaker and Evans, 1989), and based on the assumption that the original fluid was pure CO₂. It is noteworthy to recall that calculated pressures correspond also to the internal fluid pressure in the fluid inclusion when it reached the surface at magmatic temperatures (Fig. 1). It is a real wonder how some of these deep mantle fluid inclusions could survive similar overpressures, owing to a number of factors such as the small size of the inclusions, the equilibrium shape of the cavity (negative crystals), and the rapid ascent and cooling in the host magma (Hall and Bodnar, 1989; Wanamaker and Evans, 1989; Hansteen and Klügel, 2008).

The preservation of mantle fluid inclusions is controlled by the ascent history of the xenoliths in the host magma. Great source depths, slow ascent rates, and high magma temperatures favor fluid inclusion density resetting to lower values in mantle xenoliths (Hansteen and Klügel, 2008; and references cited therein). Experimental studies have shown that the threshold pressure required for brittle (i.e., decrepitation) or plastic failure (i.e., stretching) of CO₂-rich fluid inclusions in olivine increases with decreasing

inclusion size (Hall and Bodnar, 1989; Wanamaker and Evans, 1989). Larger fluid inclusion cavities, more than 5–10 μm in size, either re-equilibrate to lower densities by partial fluid leakage, or are “empty”, filled by atmospheric air after the departure of deep fluids. Thus, the extreme fluid densities ($\geq 1 \text{ g/cm}^3$) measured in many CO_2 -rich fluid inclusions from mantle xenoliths are consistent with lithostatic pressures at lithospheric depths relevant to magma genesis, demonstrating that free fluid phases were trapped prior or during the peridotite partial melting events, which generated the eruptive lavas.

Mantle derived CO_2 -rich fluids may help to contribute to the gradual rise of successive magma chambers en route towards the surface, finally migrating into the magma chamber nearest the surface (7–3 km depth), to be then released into the atmosphere during volcanic eruptions (cf., Zanon et al., 2003; Peccerillo et al., 2006; Hansteen and Klügel, 2008). The ultimate CO_2 source, however, must be very deep in the lithosphere or even in the asthenosphere. Microdiamonds have been discovered by Raman spectroscopy at Salt Lake Crater in Oahu, Hawaii, in the densest mantle CO_2 -rich fluid inclusions so far reported, indicating that they originated in the asthenospheric mantle in the diamond stability field at depths greater than 150 km (Frezzotti and Peccerillo, 2007).

3. Carbonate inclusions, and carbonate- CO_2 fluid inclusions

In mantle peridotites, one salient feature of CO_2 -rich fluid inclusions is that they can occur associated with, and/or contain, carbonate minerals (e.g., calcite, dolomite, magnesite). The textural relationships between CO_2 -rich fluid inclusions and carbonates are, however, complex. Whether carbonates exist that did not have an

epigenetic origin is, in many cases, ambiguous. Carbonates may easily form through late stage post-trapping host mineral – fluid inclusion reactions during cooling at the surface (see sections below). Similarly, if liberated by fluid inclusion decrepitation during the late stage of decompression, CO_2 -rich fluids will be highly reactive towards any kind of late hydrothermal fluids, and may quickly react to form late stage, hydrothermal carbonates, even in peridotites that look quite pristine. This is notably the case for a number of isolated tiny carbonate aggregate crystals occurring in many basaltic phenocrysts. Any trace of fluid has disappeared, but the rounded shape suggest that these carbonate aggregates occur at the place of former fluid inclusions, which ruptured when the rock was close to the surface.

The same possibly has been described for carbonate aggregates in mantle xenoliths from Spitsbergen interpreted as being the result of mantle immiscibility processes between carbonate-rich and silicate-rich melts (Amundsen, 1987), though this still to be unanimously accepted by the scientific community. The extreme facility to produce late-stage, secondary carbonates in peridotites is probably at the origin of the conventional wisdom regarding the ‘virtual absence of mantle-derived carbonates in xenoliths’ (Canil, 1990). In the temperature range between 800 and 1100 $^\circ\text{C}$, documented by most mantle xenoliths, reaction kinetics are very fast, and carbonates co-existing with pyroxenes decompose within minutes to produce CO_2 -rich fluids during decompression.

The examples discussed above outline the susceptibility of mantle carbonates to be erased from the geological record in mantle xenoliths. It is probable, however, that a few of these ephemeral mantle carbonates can be preserved as fluid inclusions, closely related to the CO_2 -fluids (Fig. 2). Carbonates, considered to be primary mantle phases in CO_2 -rich fluid inclusions (i.e.,

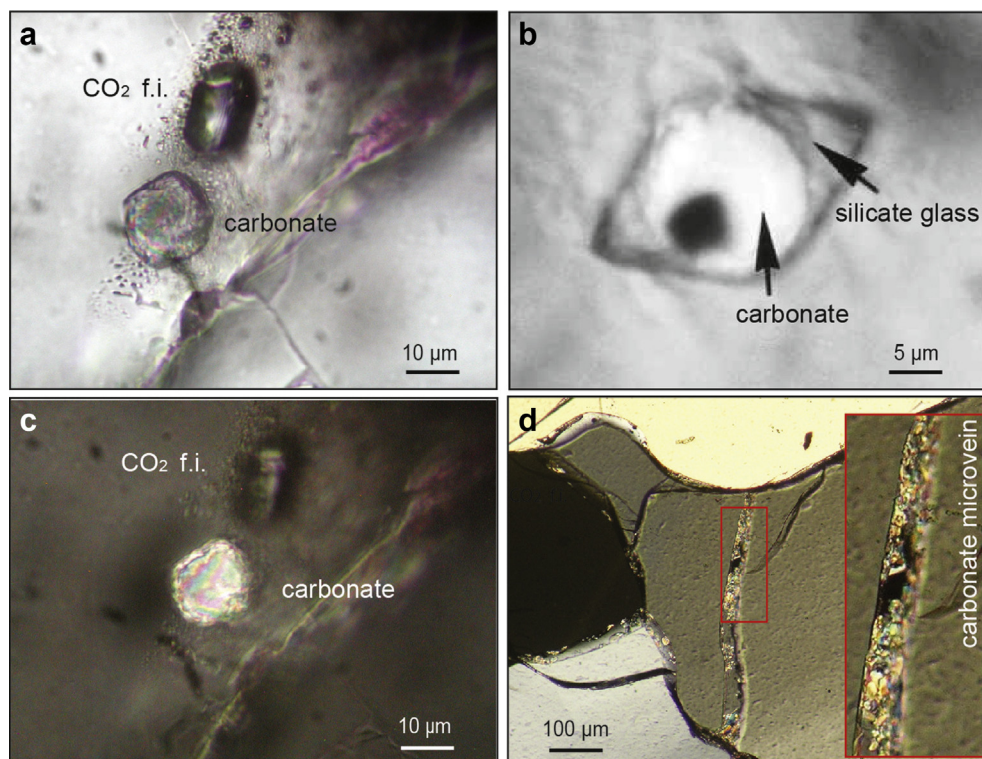
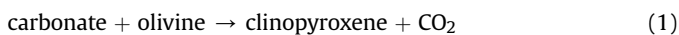


Figure 2. Microphotographs of mantle carbonates in peridotites. (a) Carbonate coexisting with a decrepitated CO_2 -rich fluid inclusion (f.i.) in olivine. Spinel lherzolite from the southern Ethiopian rift. (b) Silicate glass + carbonate inclusion in olivine. The rounded boundaries between carbonate and silicate glass indicate that, at some stage, the fluid inclusion contained two immiscible liquids. Spinel dunite from La Gomera, Canary Islands; modified after Frezzotti et al. (2002a). (c) Same than in (a) with two polarizers. (d) Intra-granular micro-veins of carbonate and glass in olivine. Inset shows that microveins consist of tiny carbonate grains and some silicate glass (black with two polarizers). Spinel lherzolites from Mt. Vulture, Italy.

precursor or syngenetic), have been described in mantle xenoliths from intraplate and extensional settings (e.g., Kerguelen, Canary, and Hawaii islands, and the East African rift; Frezzotti et al., 1994, 2002a,b, 2010; Schiano et al., 1994; Frezzotti and Peccerillo, 2007). These are micrometer-sized single calcite or dolomite crystals often with rounded shapes (Fig. 2a–c). They are often associated with silicate glass and CO₂-rich fluids (Fig. 2a and b). Carbonates of mantle origin, which form intra-granular microveins, have also been described (e.g., Mt. Vulture; Fig. 2d) (Downes et al., 2002). The textural characteristics of carbonates in many fluid inclusions from mantle rocks negate the possibility that they represent late epigenetic phases. Carbonate micro-veins are typically found along inter-granular cracks, and are always polycrystalline aggregates of sub-micron sized crystals.

In general, solid carbonates do not survive ascent at pressures lower than 2–2.4 GPa. They decompose and liberate CO₂, while reacting with some mineral host, notably olivine via the reaction:



Two eventualities may occur: (1) partial decomposition, with some carbonate crystals still being present in the outgassed CO₂ and (2) decomposition, with the complete disappearance of the “deep” carbonates due to decomposition. This corresponds to a well-known case of mantle metasomatism, probably far more common than often assumed (Coltorti and Gregoire, 2008, and references cited therein). To expand:

(1) Partial decomposition. The transition of carbonates to CO₂-rich fluids has been documented in metasomatized dunites from La

Gomera, in the Canary Islands (Frezzotti et al., 2002a). Carbonate droplets containing silicate glass ± CO₂ occur as inclusions and micro-veins in olivine (Fig. 3a). Primary carbonates are Mg-calcite ($X_{\text{Ca}} = 0.89\text{--}0.93$) and dolomite ($X_{\text{Ca}} = 0.46\text{--}0.54$), with low Na₂O. The composite carbonate inclusions (Figs. 2b and 3b) contain quenched carbonate and silicate liquid, which result from unmixing of homogeneous melt after trapping. Modeling of initial bulk compositions suggests dolomitic melts, with high silica (>10 wt.%) and H₂O, but low alkali contents. Glass micro-veins represent a residual, degassed, hydrous, mafic silicate fraction, after decarbonation. As illustrated in Fig. 3a and b, abundant short intra-granular trails of CO₂-rich fluid inclusions originating in the glass micro-vein intrude into the host crystal, suggesting carbonate late stage melt degassing.

Within single fluid inclusions, the relative amount of CO₂ and carbonate is highly variable (Fig. 4a), as one might expect for the mechanical capture of solid carbonate and CO₂-rich fluid. There are, however, some examples of amazingly constant carbonate/CO₂ fluid volume ratios, indicating that the fluid, being trapped, was a homogeneous mixture consisting of carbonate and CO₂ components. Such a case has not been observed in mantle rocks, but in lower-crustal garnet granulites from Sri-Lanka (Fig. 4b and c; Bolder-Schrijver et al., 2000). As suggested by Touret and Huizenga (2012a,b), inclusion-forming fluids originated in the mantle, and were brought into the lower crust by mantle-derived syn-metamorphic intrusions. Compared to fluid inclusions in mantle xenoliths, fluid inclusions in the granulites experienced a slower exhumation, and thus the preservation of such a relatively unstable solid-gas system was more favorable.

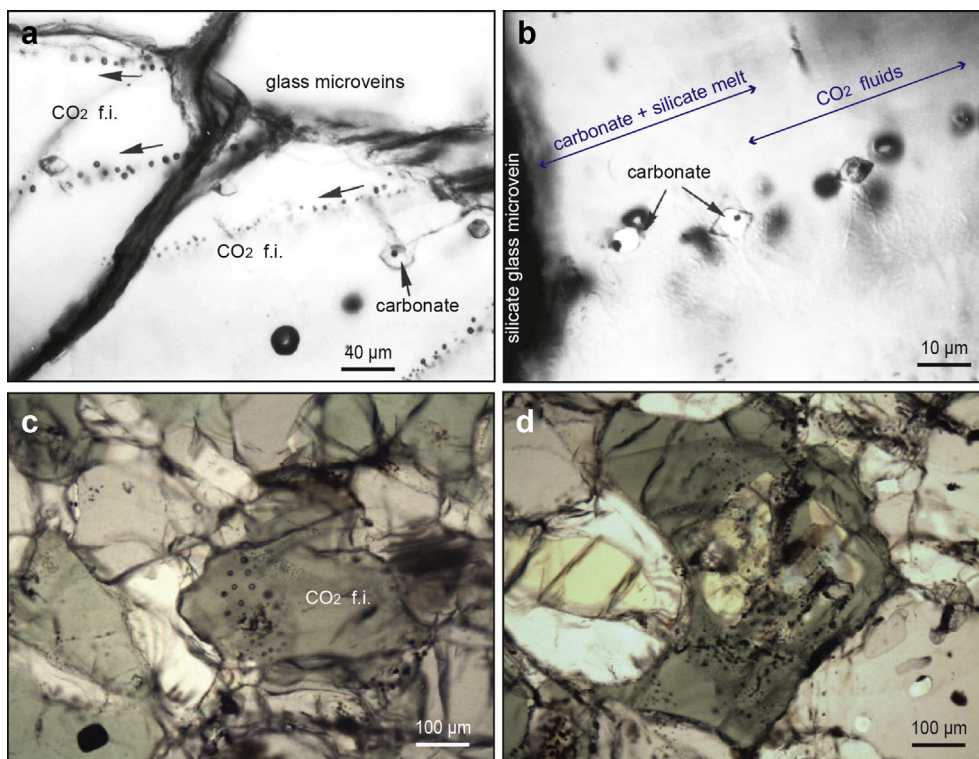


Figure 3. Textural relationships between carbonates and CO₂ inclusions in peridotites. I – Partial carbonate decomposition: (a) mixed carbonate-silicate melt inclusions and trails of CO₂-rich fluid inclusions (f.i.), originating from silicate glass micro-veins (arrows); (b) detail of a coeval carbonate and CO₂-rich fluid inclusions extending from a mafic silicate glass vein, two polarizers. Carbonate inclusions are always close to the vein, while CO₂-rich fluid inclusions occur at a greater distance within the olivine grain. Both examples are from a spinel dunite from La Gomera, Canary Islands (Frezzotti et al., 2002a). II – Complete carbonate decomposition: (c) CO₂-rich fluid inclusions (black dots) occur exclusively in the clinopyroxene (greenish). The surrounding olivine crystals (colorless) are completely inclusion-free; (d) a cluster of CO₂-rich fluid inclusions (dark contoured circles). In the center an indistinct, badly crystallized and subidiomorphic (lozenge) zone (arrow), interpreted as the remnant of a former carbonate inclusion. Both examples are from Iherzolite, Lake Nyos, Cameroon (Touret et al., 2010).

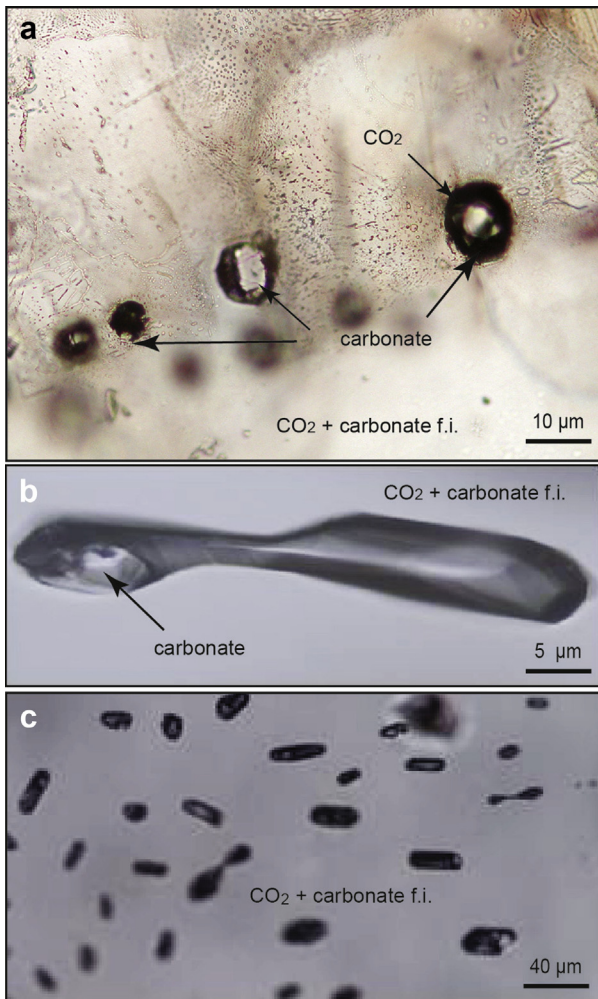


Figure 4. Carbonate/CO₂ volume relationships inside fluid inclusions. (a) Variable carbonate/CO₂ ratios in fluid inclusions in spinel lherzolites from the Ethiopian rift. (b) and (c) Constant carbonate/CO₂ volume ratios in fluid inclusions in granulites from Sri Lanka, modified after Bolder-Schrijver et al. (2000).

(2) Complete decomposition. The growing evidence for widespread mantle metasomatism with a distinct carbonatite isotope and trace element signature indicates that, in general, carbonate melts react with peridotite minerals until the complete disappearance of carbonates (cf., Wallace and Green, 1988). Good evidence for this process can be found in the relative abundance of fluid inclusions in the different rock-forming minerals. From our experience, it is rare that mantle minerals, either major (i.e., olivine and pyroxenes) or accessories (e.g., apatite) contain the same number of early fluid inclusions (primary, or the far more abundant pseudo-primary). This can be easily explained if the rock has a cumulative origin, where some minerals (eventually olivine or accessories) crystallized in presence of a fluid phase, while other did not. The relatively rare examples of selective fluid inclusion abundances in olivine can be explained in this manner. The frequent occurrence of fluid inclusions in pyroxene, on the other hand, requires a different explanation.

Spinel lherzolites occurring in the mantle xenoliths found at Lake Nyos (Cameroon) are in this respect very typical (Touret et al., 2010). Fluid inclusions occur exclusively in clinopyroxene (Fig. 3c), whereas the neighboring olivine grains are completely fluid inclusion-free. In some cases, groups (clusters) of fluid inclusions

occur around a badly crystallized, roughly lozenge-shaped zone, interpreted as the possible remnants of a former carbonate melt inclusion (Fig. 3d). Such a hypothesis is supported by the regular decrease of the clinopyroxene Mg-number around this zone, possibly due to the influence of Fe liberated during the destabilization of the carbonate. The mineralogy and trace element pattern of the Lake Nyos lherzolites clearly indicate mantle metasomatism (Teitchou et al., 2011), in line with the above observation.

The examples described above are relatively rare, and most mantle xenoliths contain only CO₂-rich fluid inclusions. However, these examples testify that “deep” carbonate melts are parental to the CO₂ found in many mantle xenoliths. Furthermore, they outline the processes occurring during metasomatic reactions of carbonates in the upper mantle, which result in outgassing and liberation of CO₂ fluxes.

4. H₂O in mantle fluid inclusions

One common misperception about fluid inclusions in ultramafic xenoliths is that they do not contain H₂O. In peridotites, data traditionally report CO₂ as the major, if not the only, component of fluid inclusions (e.g., Roedder, 1984; Andersen and Neumann, 2001 and references cited therein), even though aqueous fluids have been described in some peridotites from different geodynamic settings (e.g., Trial et al., 1984; Scambelluri et al., 1997; McInnes et al., 2001; Frezzotti et al., 2010, 2012b; Kawamoto et al., 2013). Thermodynamic equilibria, however, predict H₂O as the main fluid component in carbon under-saturated C-O-H mantle fluids at $P = 2\text{--}3$ GPa, for oxygen fugacities (f_{O_2}) \geq QFM buffer (Huizenga, 2001, 2005; Zhang and Duan, 2009, 2010). The chemistry of gases contained in, or discharged from basaltic magmas, and the chemical composition of metasomatic mantle phases (e.g., phlogopite, amphibole, and apatite) also points to an aqueous component in mantle CO₂-rich fluids (Murck et al., 1978; Marty and Tolstikhin, 1998; Marty and Zimmermann, 1999; O'Reilly and Griffin, 2000; Oppenheimer et al., 2011).

The possible presence of water in deep CO₂-rich fluid inclusions was long overlooked due to the lack of a robust analytical approach. Until recently, water in fluid inclusions has been revealed by microscopic analyses only. Most mantle fluid inclusions, however, are small (<5–10 μm in size) and have regular shapes (Fig. 5a). Both factors help to strongly limit the optical resolution, especially in dense, often colored peridotite minerals (cf., Roedder, 1984). In recent years, improved analytical capabilities, particularly increased sensitivity and spatial resolution of Raman and FT-IR micro-spectroscopy, have, in part, solved this problem (Frezzotti et al., 2012a, and references cited therein). Although not yet widely applied, spectroscopic analyses have revealed subordinate amounts of water in some CO₂-rich fluid inclusions from peridotites (Fig. 5b). For example, about 10 to 30 mol% molecular H₂O has been measured inside apparently pure (under the petrographic microscope) CO₂-rich fluid inclusions in mantle xenoliths from the Ethiopian plateau area (Frezzotti et al., 2010, 2012b, and references cited therein).

A further indication for a possible aqueous component in shallow-mantle fluids comes from the increasing evidence that, in some cases, the CO₂-rich composition of fluid inclusions results from post-trapping dehydration (Fig. 6). Spectroscopic studies have demonstrated that molecular H₂O can passively diffuse from the fluid inclusions into the host mineral, and/or react with the surrounding mineral host to form (step) daughter mineral phases (mainly hydrous Mg-rich silicates and carbonates; Fig. 6) (Hidas et al., 2010; Frezzotti et al., 2012b; Kawamoto et al., 2013). Passive H₂O diffusion from H₂O-CO₂ fluid inclusions was previously recognized in quartz by experimental studies, driven both by H₂O

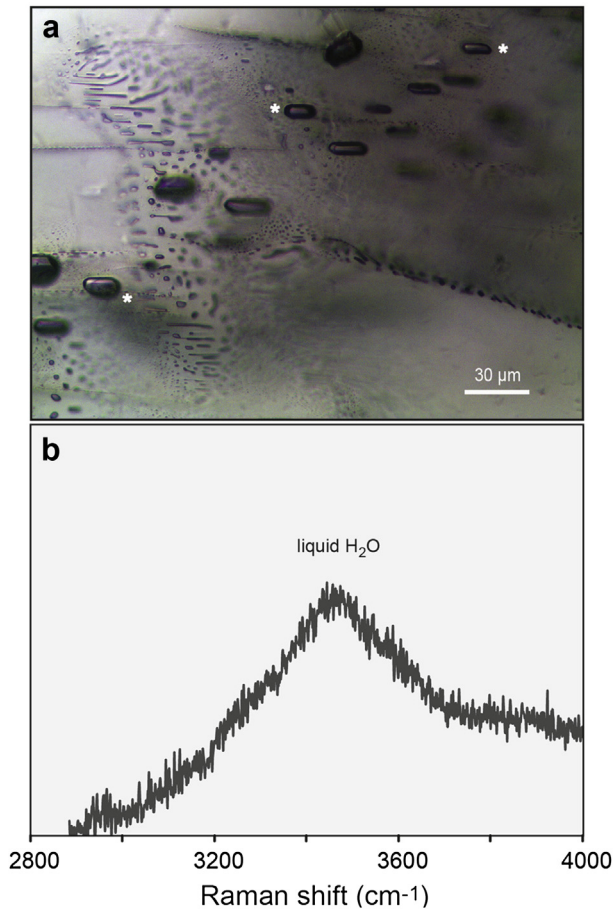


Figure 5. Raman detection of optically hidden liquid H₂O in mantle fluid inclusions. (a) Trail of fluid inclusions in orthopyroxene. White asterisks indicate those fluid inclusions where liquid water was revealed by Raman micro-spectroscopy. (b) Raman spectrum of liquid H₂O rimming CO₂ in a fluid inclusion from Fig. 2a (high center). Spinel lherzolites from the Ethiopian plateau area, modified after Frezzotti et al. (2010).

fugacity gradients and by the formation of micro-cracks and dislocations, induced by differential pressures during the exhumation of the rocks (Sterner and Bodnar, 1989; Hollister, 1990; Bakker and Jansen, 1991). Although rarely taken into account in mantle studies, this process has also been experimentally proven to occur in fluid inclusions from xenolithic olivine, during decompression at high temperatures (Wanamaker and Evans, 1989).

Fig. 7 illustrates the effects of fluid inclusion dehydration trends in mantle minerals. The FT-IR synchrotron map of H₂O distribution in xenolith olivine from the Ethiopian plateau (Fig. 7a) outlines the exponential increase of bonded hydrogen approaching a CO₂-rich fluid inclusion trail, which forms symmetrical water enrichment haloes parallel to the fluid inclusions' trail direction (Fig. 7b). In these areas, local hydration of olivine occurs, confirmed by the detection of minute talc grains (Fig. 7c). At high *P* and *T*, dehydration of the original CO₂-H₂O fluids in inclusions trapped in mantle xenolith minerals should occur very quickly through lattice defects and micro-fractures in the host minerals under conditions of decreasing *P* and *f*_{H₂O} during ascent in host magma (Mackwell and Kohlstedt, 1990; Viti and Frezzotti, 2000, 2001). One relevant consequence of the dehydration phenomena is that pressure data derived from these fluid inclusions is robustly underestimated, since they merely reflect re-equilibration processes and not the original trapping conditions of the mantle CO₂-H₂O. Further discussion on dehydrated fluid inclusion density corrections can be found in Hansteen and Klügel (2008).

Although these observations suggest that water can be a relevant component in mantle fluids, the paucity of fluid inclusions still containing water makes it difficult to estimate the primary water content in CO₂-rich fluid phases. An indirect insight into the potential water budget of mantle fluids can be gained by thermodynamic modeling of observed reactions between fluid inclusions and the surrounding minerals. As shown in Fig. 8, at *T* ≤ 700 °C and *P* variable between 1 and 0.1 GPa, the formation of talc + magnesite in one fluid inclusion reacting with orthopyroxene host (e.g., MFSHC system; Connolly, 1990) is possible if trapped CO₂-H₂O fluids contained 0.1 ≤ *X*_{H₂O} ≤ 0.5 (Frezzotti et al., 2012b). Higher *X*_{H₂O} in the fluid would be required to form serpentine. A number of these reactions, occurring at the fluid inclusion interface, have been

Fluid Inclusion Dehydration Trend

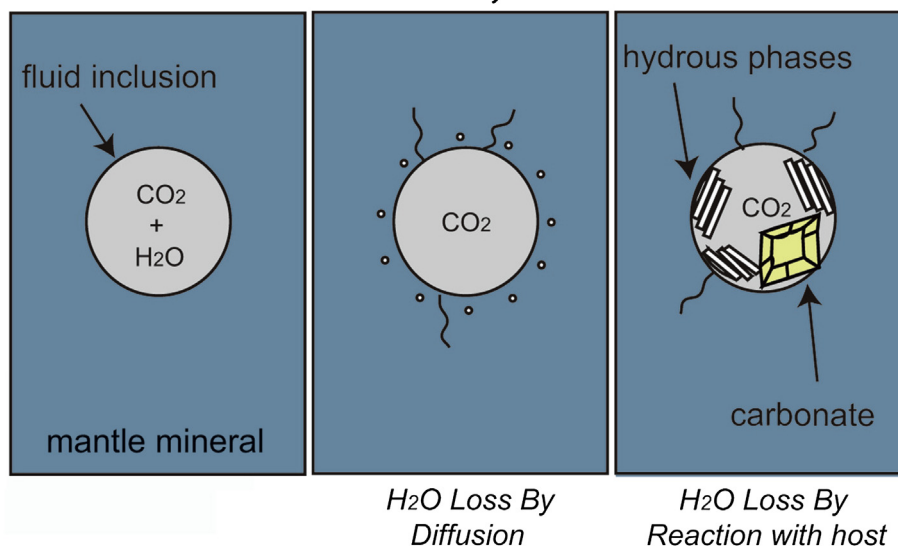


Figure 6. Post-entrapment dehydration trend of mantle fluid inclusions. Passive molecular H₂O diffusion, and/or reaction with the mineral host to form stepdaughter (in the sense of Roedder, 1984) hydrous silicate and carbonate minerals.

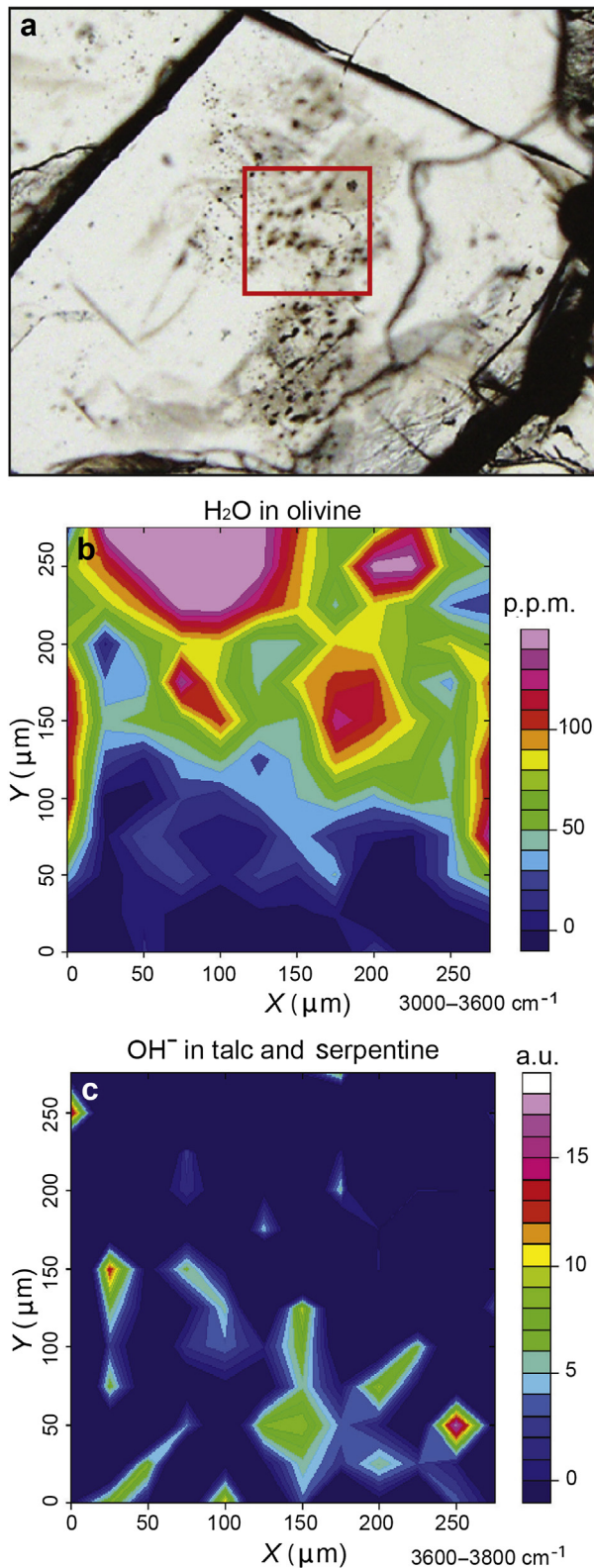


Figure 7. Synchrotron FT-IR imaging of H₂O distribution around CO₂-rich fluid inclusions in mantle olivine. (a) Microscopic overview of the investigated area, one polarizer. CO₂-rich fluid inclusions appear on the microphotograph as black dots. (b) FT-IR absorbance map in the 3000–3600 cm⁻¹ region, and calculated ranges of the H₂O content with a precision of 10's of ppm. The color scale is proportional to OH⁻ enrichment in olivine (increasing from blue to pink). (c) Distribution map of OH⁻ absorbance for talc and serpentine in the 3600–3800 cm⁻¹ region, which demonstrates the presence of hydrous Mg-silicate in olivine. a.u.: arbitrary units. Spinel lherzolites from the Ethiopian plateau area, modified after Frezzotti et al. (2010).

described in the literature (Fig. 9a; e.g., Hirai and Arai, 1987; Frezzotti et al., 2002b; Hidas et al., 2010; Kawamoto et al., 2013). For example, talc, magnesite, chlorides, silica, and gypsum are present in CO₂-rich fluid inclusions in orthopyroxene from Italian mantle xenoliths (Fig. 9). Microstructures clearly indicate that relatively large magnesite and talc crystals formed through reaction with the enclosing mineral (Fig. 9b,f and g), while chloride, sulfate, and silica precipitated from the fluid as tiny aggregates during cooling and decompression (Fig. 9b–e).

In conclusion, the possible occurrence of a subordinate aqueous fluid component in the mantle cannot be denied, even if no trace is found in most mantle xenolith fluid inclusions. Again, the similarity with lower crustal granulite-facies fluids is striking. They are also, the dominant fluid inclusions are CO₂-rich and resemble the same fluid inclusions found in mantle rocks. The occurrence of brines has mostly been documented by the traces that they have left in the rocks, notably along grain boundaries (e.g., Touret and Nijland, 2013). It cannot be excluded that, similar to CO₂, a portion of these granulite-facies brines derive from the mantle (Glassly et al., 2010). However, at least in some regions (e.g. Bamble, southern Norway), brine fluid inclusions are especially abundant in favorable lithologies (meta-evaporites), which indicates that local derivation can be dominant. Observations of fluid inclusions in granulites support the hypothesis for two distinct, immiscible fluids. Is this also the case in the mantle?

5. Mantle CO₂ and brines, one or two fluids?

Fluid inclusion data provide evidence that Cl, Si, S, Ca, K, and Na are the major solute components in aqueous mantle fluids (Fig. 9c; Scambelluri and Philippot, 2001; Frezzotti et al., 2010; Kawamoto et al., 2013). Calculated solute concentrations span a wide range from 5 to 50 wt.% in NaCl equivalent (i.e., saline brines), with the least chloride contents (<15 wt.% NaCl eq.) in those fluid inclusions with the highest X_{CO₂}. This semi-quantitative trend in element solubility deduced from the fluid inclusion data is in agreement with a number of distinct arguments, including:

- (1) Consistency with experimental results, which predict alkalis to be the most soluble species at high *P* and *T* (3 GPa and 1300 °C), followed by Cl, Si, and Ca, while Mg and Fe are relatively less soluble (e.g., Eggler, 1987; Brenan et al., 1995; Kawamoto et al., 2004; Manning, 2004).
- (2) Relatively high Cl- or F- content in many hydrous minerals from metasomatised mantle peridotites (e.g., phlogopite, pargasite).
- (3) A low salinity H₂O phase, most commonly below 2–3 mol% NaCl equivalent (salting-out effect; Roedder, 1984), in CO₂-bearing inclusions found in crustal rocks (mixed H₂O-CO₂ fluid).
- (4) If distinct from CO₂-bearing fluids, high-water activity fluids would immediately promote melting of mantle peridotite, and then be transferred to upper levels by rising magmas.

Because of the complex behavior of the ternary CO₂-H₂O-NaCl fluid system at high *P* and *T*, the hypothesis of two distinct immiscible fluids at mantle depths must be considered. As discussed in the previous sections, the relative rarity of an aqueous component in CO₂-rich fluid inclusions can in part be explained by passive water diffusion, and/or by reaction with enclosing minerals (Fig. 6). An alternative or additional possibility is that the CO₂-rich fluid composition may be derived by selective CO₂ entrapment due to immiscibility processes at high pressure, in which case a carbonic fluid phase forms and moves separately from a saline brine (Johnson, 1991; Gibert et al., 1998; Heinrich, 2007; Touret and Huizenga, 2012b). Touret (1985) first suggested that at upper

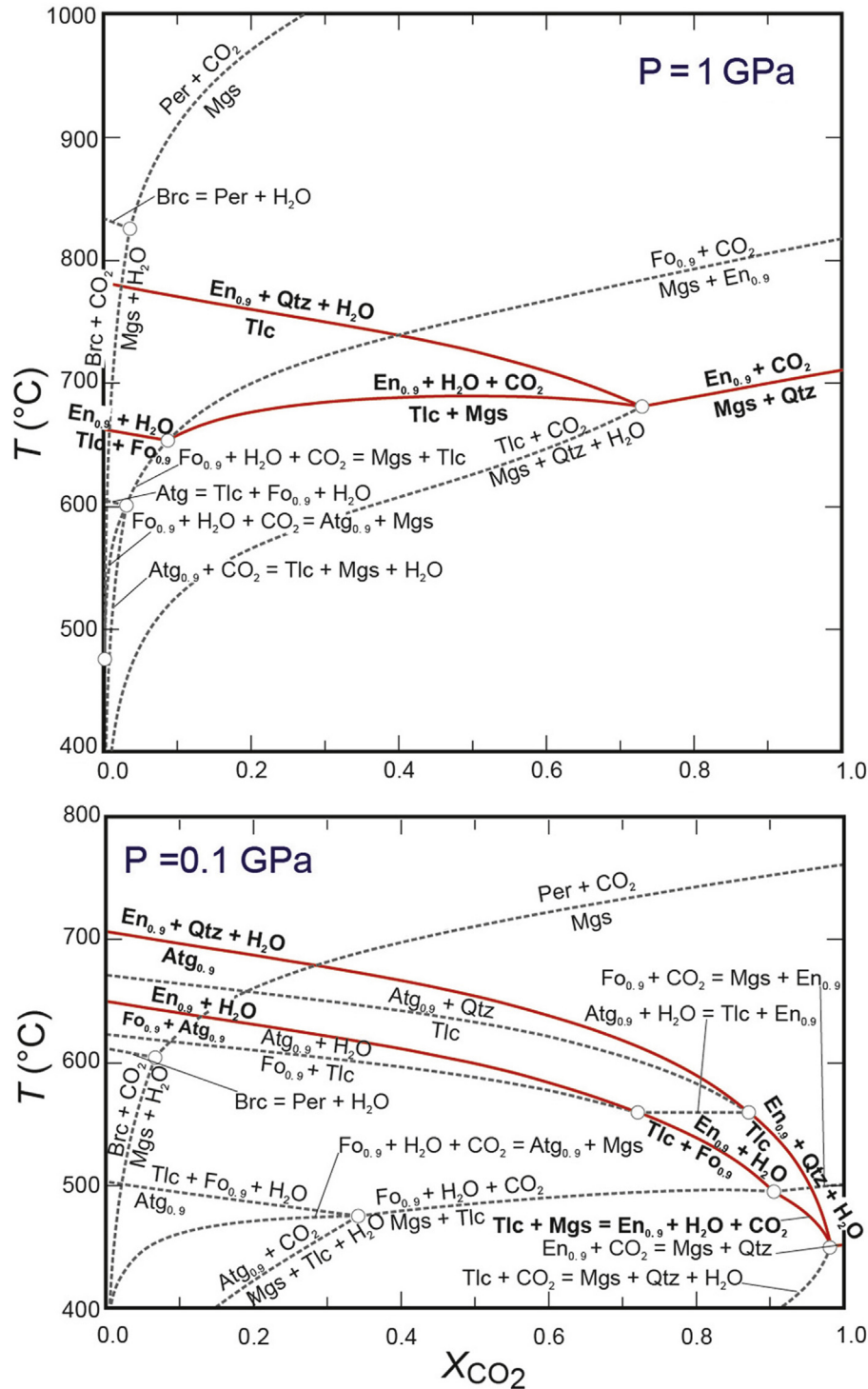


Figure 8. $T - X_{\text{CO}_2}$ sections at 1.0 and 0.1 GPa in the MgO-FeO-SiO₂-H₂O-CO₂ model system with $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.9$, modified after Frezzotti et al. (2012b). White dots are the invariant points. Red solid curves represent the reactions between H₂O-CO₂ fluids trapped in the fluid inclusions and the surrounding magnesian orthopyroxene. In all reaction equations, the high- X_{CO_2} assemblage is on the right side.

mantle and lower crustal conditions, the large miscibility gap existing in the ternary NaCl-CO₂-H₂O fluid system may result in two coexisting immiscible fluid phases, namely CO₂ and brines. There is no doubt that immiscibility in the CO₂-H₂O-NaCl system may occur at high P , and a number of studies have previously proposed two-phase fluid conditions at lower crustal and upper mantle depths (e.g., Skippen and Trommsdorff, 1986; Trommsdorff

and Skippen, 1986; Newton et al., 1998; Heinrich et al., 2004; Newton and Manning, 2010).

Although immiscible CO₂-rich and saline brine fluid inclusions have been described in lower-crustal rocks (e.g., Touret and Huizenga, 2012a,b), examples are lacking from mantle peridotites. Most likely, the general absence of brine fluid inclusions in mantle minerals is due to the different wetting behavior of these two fluid

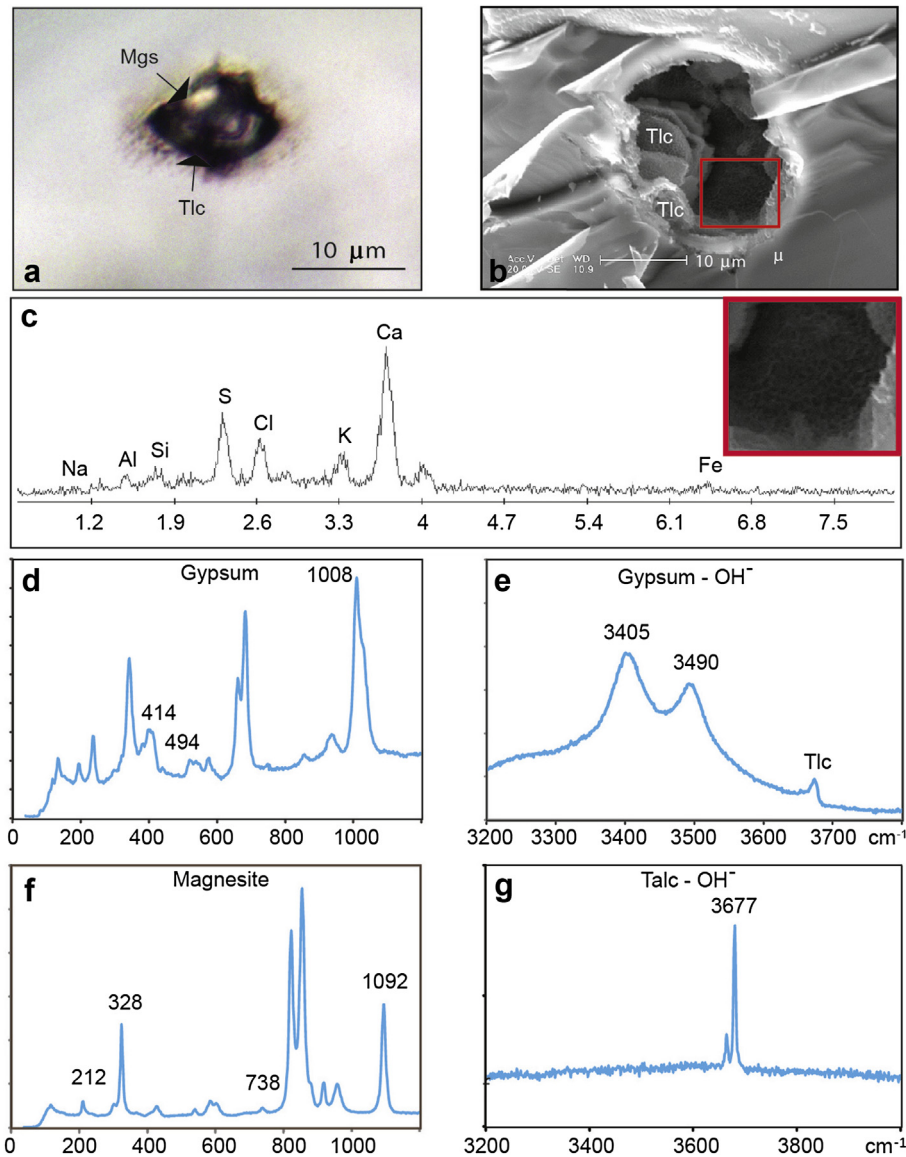


Figure 9. Raman micro-spectroscopy and EDS-EDAX analyses of reacted mantle fluid inclusions. (a) Dehydrated fluid inclusion in olivine (spinel lherzolite of the Ethiopian plateau). The fluid inclusion contains liquid + vapor CO₂, talc (Tlc), and magnesite (Mgs). (b) Electron microphotograph of open fluid inclusions in orthopyroxene (spinel pyroxenite from Sardinia, Italy). Fluid inclusion walls are coated by talc and by a thin microcrystalline patina. (c) Qualitative EDS-EDAX chemical analysis of the patina shown in b (inset image). (d)–(g) Main Raman modes of mineral phases inside fluid inclusions: (d) gypsum; (e) OH⁻ in gypsum; (f) magnesite; (g) OH⁻ in talc. Unlabeled peaks refer to the enclosing minerals. Modified after Frezzotti et al. (2012b).

phases at mantle conditions (Gibert et al., 1998). This may cause preferential trapping of 'immobile' CO₂ as fluid inclusions, while 'mobile' aqueous brines may migrate through the lithosphere and be consumed through metasomatic reactions. As proposed by Touret (1995): "the other fluid (water) is squeezed out and not recorded in fluid inclusions". One possible example for two-phase fluid conditions is illustrated in Fig. 10, where coeval CO₂-rich fluid inclusions and Cl-pargasite grains are distributed along intra-granular trails in clinopyroxene from a hydrous peridotite from the Ethiopian plateau (Fig. 10a; Frezzotti et al., 2010). The Cl-pargasite – CO₂-rich fluid assemblage in a single micro-fracture probably results from two immiscible precursor fluids, i.e. a reacting brine and high density CO₂ (Fig. 10b).

The effects of phase separation in the ternary CO₂-H₂O-NaCl system are of tremendous significance for mantle processes since they influence the capacity of element mass transfer and the

density of the two coexisting immiscible fluids. In addition, formation of high salinity brines, through immiscibility in the CO₂-H₂O-NaCl system, would reduce the H₂O activity in fluids, which has implications for mantle hydration and partial melting processes.

6. Fluid origin and metasomatism: from carbonate-rich melts to CO₂ ± brine fluids

The mantle xenolith fluid inclusion data reviewed above provides a foundation for the interpretation of the geological role of CO₂-rich fluids in mantle metasomatic processes. One possibility for the origin of CO₂-rich fluids ± brines and carbonatitic fluids in the lithosphere, unrelated to basalt degassing, is that they might be derived from deeper mobile carbon-rich fluid or melt phases through outgassing processes. There is an interesting parallel

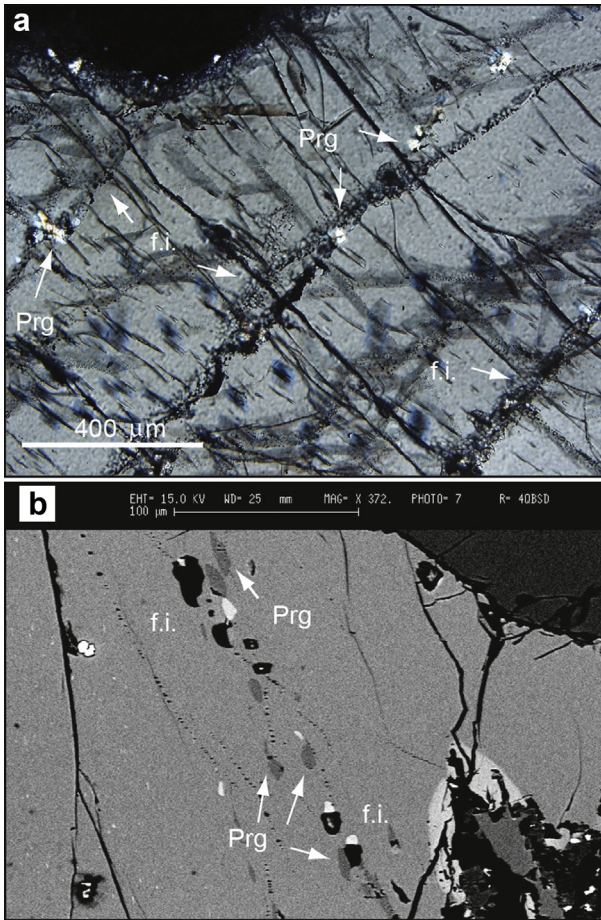


Figure 10. (a) Trail-bound coeval fluid inclusions (f.i.) and pargasite grains (Prg) in clinopyroxene from hydrous peridotites, two polarizers. (b) Back scattered electron image of f.i. (black) and Prg (dark gray) distribution. Spinel inclusions are also visible (white). Note that the Prg inclusions have the same chemical composition as the metasomatic phase in the peridotites. Spinel lherzolites from the Ethiopian plateau area, modified after Frezzotti et al. (2010).

between the shallower peridotite xenolith evidence for $\text{CO}_2 \pm$ brine fluids, and the evidence from deeper diamonds and kimberlites for $\text{CO}_2\text{-H}_2\text{O-Cl}$ -rich fluids/melts. In fibrous diamond, the composition of nanometric fluid inclusions, although variable, can be referred to three end-members (Navon et al., 1988; Izraeli et al., 2001; Klein-BenDavid et al., 2004, 2007): (1) a hydrous-silicic end-member, rich in Si, H_2O , and alkalis; (2) a carbonatitic end-member, rich in CO_3^{2-} , Mg, Ca, Fe, and alkalis; and (3) a hydrous-saline end-member, rich in H_2O , Cl, K, and Na. Thus, $\text{CO}_2 \pm$ brine fluids deep in the lithosphere, or even in the asthenosphere, can testify for dissociation and outgassing of deeper hydro-saline carbonate (silicate) melts rising through the mantle, at pressures below 2–2.4 GPa.

Carbonate-rich melts (i.e., carbonatitic and carbonated silicate melts) are stable in the lithosphere and asthenosphere. They can be generated by different processes, including: (1) partial melting of a carbonated peridotite, (2) metasomatic reactions between a silicate-carbonate fluid/melt and mantle peridotite, and (3) local immiscibility processes in a carbonate-silicate melt (e.g., Schrauder and Navon, 1994; Schrauder et al., 1996; Lee and Wyllie, 1998). Experimental studies have shown how the depth and the degree of melting of carbonated peridotites govern the concentration of carbon and other incompatible elements in generated magmas (e.g., Wallace and Green, 1988; Dalton and Presnall, 1998; Dasgupta and Hirschmann, 2006, 2007a,b; Dasgupta et al., 2007). According

to Gudfinnsson and Presnall (2005), at lithospheric $P\text{-}T$ conditions (1000 °C, >2 GPa), very low degrees of partial melting of carbonated peridotites will generate carbonatitic melts (Fig. 11a).

Such melts are likely to be extremely enriched in incompatible major and trace elements (e.g., Green and Wallace, 1988), and record the lowest viscosity of any magma types, having very low interfacial energies with respect to mantle minerals (Dobson et al., 1996). Dihedral angles (θ) are in the range of 25–30°, and depend only slightly on temperature or pressure (Watson and Brenan, 1987; Watson et al., 1990). These properties allow very low fractions of carbonate-rich melts to rise through an interconnected grain boundary network, at very low porosities (0.1%), to cause widespread metasomatism in peridotites (Fig. 11b), resulting in an enriched lithosphere (i.e., crystallization of carbonates \pm hydrous minerals such as amphibole and phlogopite, strong enrichment in LREE and in some incompatible trace elements; Ionov et al., 1993). A nice example of alkali- and carbonate-rich melts permeating the continental lithosphere, outside the diamond stability field at depths of about 110 km, is preserved by melt inclusions in polymict mantle xenoliths from the Bultfontein kimberlite, Kimberley, South Africa (Giuliani et al., 2012). These inclusions consist of carbonates (magnesite, dolomite, and alkali-rich carbonates), with subordinate silicates (kalsilite, phlogopite, and olivine), phosphates, chlorides, and sulfates, which suggests a composition enriched in CO_2 , Mg, Ca, K, Na, with subordinate SiO_2 , P, S, F, and Cl.

As discussed above, most mantle carbonate-rich melts have a limited duration since they will be consumed. Decarbonation reactions offer an easy way to outgas almost unlimited quantities of CO_2 (Fig. 11b), as proposed to occur in peridotites. It must be noted that in this scenario the amount of CO_2 , which can be transported by magmas rising towards the surface is not at all constrained by its solubility in the magma. Some kimberlites (e.g., Slave Craton, Northwest Territories, Canada), with geochemical carbonatitic affinities (i.e., LREE, Sr, Ba, and, P), contain up to 10 to 17 wt.% CO_2 (Price et al., 2000).

The fact that fluid inclusions can be formed at any step of the ascent shows that these magmas are systematically CO_2 -saturated, and thus able to transport huge amounts of CO_2 in the form of bubbles within the magma. Carbonate-rich melts may eventually reach the Earth's surface, provided that the eruption is fast and violent enough, as in the case for kimberlites (Bodinier et al., 2004), or that the Na content of carbonate-rich melt is high enough (i.e., natro-carbonatites), as in the case for Ol Doinyo Lengai (Genge et al., 1995). Thus, the major control for the finding of primary carbonate-rich melts in mantle rocks is not their stability but, rather, their preservation during mantle evolution and subsequent magmatic eruption. Entrapment as inclusions may protect carbonate-rich melts from reacting with mantle minerals during the ascent processes in the host magmas. All together, CO_2 , brines, and carbonate inclusions provide evidence for a model of deep carbon mantle outgassing, which can be seen as an alternative to basaltic magma CO_2 degassing (Fig. 11b). In this regard, the deep carbonate- CO_2 -diamond association preserved in fluid inclusions in garnet pyroxenites from Hawaii could be an example of mantle CO_2 fluxes in the lithosphere discussed below.

6.1. Carbonate melt decomposition and fluxing of CO_2 in the region of diamond growth

The transition from carbonate-rich melts to CO_2 -rich fluids has been described in the oceanic lithosphere beneath Hawaii (Frezzotti and Peccerillo, 2007). It is based on the association of $\text{CO}_2\text{-H}_2\text{O-Cl-S}$ fluids, carbonate, and diamond preserved in fluid inclusions for garnet pyroxenite xenoliths, which are taken from the post-erosional stage Honolulu volcanics (<1 Ma) at Salt Lake

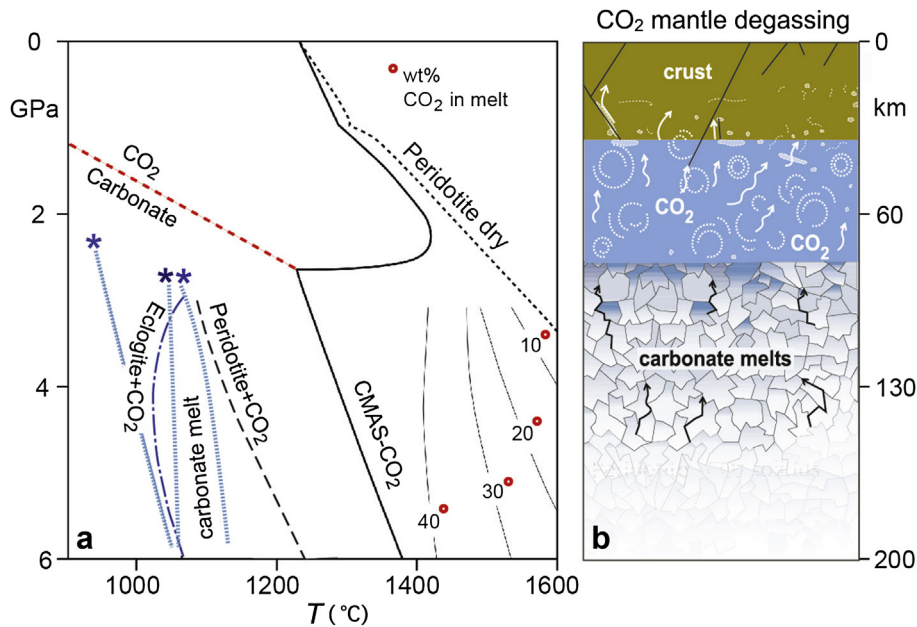


Figure 11. Schematic model of CO₂ mantle degassing via carbonate melts. (a) Effects of CO₂ on the solidus for carbonated lithologies in the mantle. Different estimates from the peridotite – CO₂ solidus are reported: CMA-S – CO₂ after Dalton and Presnall (1998), and Gudfinnsson and Presnall (2005), and Peridotite + CO₂ (2.5 wt.%) after Dasgupta and Hirschmann (2006). Peridotite dry solidus in the CMA-S system is after Gudfinnsson and Presnall (2005). Eclogite + CO₂ solidus (dry eclogite + 5 wt.% CO₂) after Dasgupta et al. (2004). Asterisks (*) with dotted lines corresponds to the KNCFMASH – CO₂ solidus (carbonated pelite + 1.1 wt.% H₂O + 4.8 wt.% CO₂) after Thomsen and Schmidt (2008). The effect of carbonates on the composition of melts generated at increasing temperature is reported as wt.% CO₂, and based on the CMA-S – CO₂ system. (b) Model of the CO₂-carbonate distribution in the lithosphere – asthenosphere system.

Crater, Koolau shield, Oahu, Hawaii. Garnet pyroxenites are cumulate rocks, consisting of clinopyroxene (diopside–augite; 40–60 vol.%), olivine, orthopyroxene, garnet, and spinel. Microdiamonds and (former) majoritic garnet have been reported in these rocks, suggesting an origin by polybaric magma fractionation at about 4.5–5 GPa in the asthenosphere (e.g., Wirth and Rocholl, 2003; Keshav et al., 2007).

In these xenoliths, the primary fluid inclusions in various mantle mineral phases (olivine, orthopyroxene, and clinopyroxene) consist of high density to super-dense CO₂-rich fluids, and a mixture of dense CO₂-rich fluids + carbonate, which may contain microdiamonds (Fig. 12a and b) Frezzotti and Peccerillo, 2007). Rare roundish single carbonate inclusions are also observed (Fig. 12a). CO₂-rich fluids in the fluid inclusions contain traces of H₂O, H₂S, and Cl. These inclusions, often distributed along preferential crystallographic orientations in the pyroxenes, were formed at mantle depth. The composition of the carbonates is variable. Dolomite occurs in CO₂ ± diamond inclusions (Fig. 12b), while both dolomite and Mg-calcite are present as rounded inclusions consisting of a single mineral grain (Fig. 12c). Whereas carbonate inclusions show high crystallinity, carbonates within the CO₂-rich fluid inclusions (±diamond) show structural disorder, as observed in decomposing carbonates. In the Raman spectra (Fig. 12b), the main carbonate vibration (1098 cm⁻¹ for dolomite) results in wide FWHM (full width of the Raman peak at half maximum height), which is indicative of low crystallinity (compare with the Mg-calcite spectrum in Fig. 12c).

Rounded dolomite inclusions associated with CO₂ and diamond (Fig. 12a) preserve a carbonate-rich melt phase that was present at high pressures in the mantle beneath Hawaii. Reduction of carbon to form diamond suggests that redox carbon-freezing reactions should have occurred during metasomatic processes. The association of structurally disordered carbonate with CO₂ and diamond could result either by trapping an outgassing carbonate melt, or by decrepitation of deep carbonate-rich melt inclusions during

decompression. In either case, these inclusions contain a contribution from a mantle metasomatic carbonate-rich melt phase and give evidence for the possibility that massive CO₂-rich fluid fluxes could be generated in the lithosphere beneath Hawaii.

7. Mantle CO₂ degassing

Mantle CO₂ degassing is a widespread phenomenon with different regimes, which depends on the time scale. This includes paroxysmal-instantaneous during volcanic eruption; paroxysmal-long duration (a few millions years) during major metamorphic episodes of peak metamorphism, typically inducing supercontinent amalgamation; or quiet, during remission periods between volcanic eruptions. Geodynamic settings for all these cases are in some way related to subduction, either active in the case of volcanism, or passive (post-subduction extensional rebound) during metamorphism. With respect to the present changes in global climate, and because of their short geological time range, the biological/physical carbon cycle is the major biogeochemical cycle considered to play an important role in the movement of carbon in and out of the crust, ocean, and atmosphere through the processes of photosynthesis and respiration. However, even though CO₂ emission from the deep Earth may be trivial compared to anthropogenic emissions (Gerlach, 2011), evaluation of natural degassing of CO₂ is important for any model of the geochemical carbon cycle.

The Earth's mantle represents the largest carbon reservoir in the planet, containing three to six orders magnitude more carbon than is stored in the atmosphere-ocean system, and one to one hundred times more than that stored in the earth's crust (Sleep and Zahnle, 2001; Coltice et al., 2004). Incorporation of carbon into the mantle is continuously provided by subduction processes. Experimental research has shown how melting of subducted oceanic crust may extract carbon at mantle lithospheric depths, whereas preservation of carbonate minerals may allow transport of carbon to the transition zone and/or to the lower mantle (e.g., Molina and Poli, 2000;

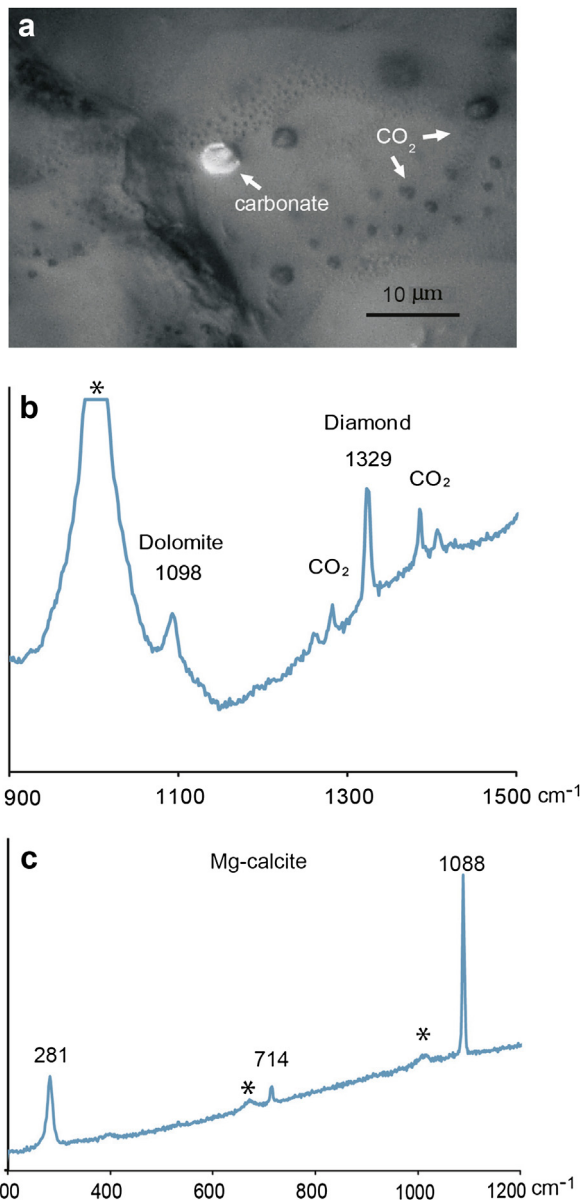


Figure 12. (a) Rounded Mg-calcite inclusion within a trail of high-density and super-dense CO₂ fluid inclusions in clinopyroxene from garnet pyroxenites, Oahu, Hawaii, two polarizers. (b) Raman spectrum of dolomite (1098 cm⁻¹) within a CO₂ + diamond (1331 cm⁻¹) inclusion in clinopyroxene Cpx. The wide FWHM (full width of the Raman band at half maximum band height) from the main dolomite Raman vibration at 1098 cm⁻¹ testifies for the poor crystallinity. (c) Raman spectrum of a rounded Mg-calcite inclusion in clinopyroxene. Asterisks indicate host clinopyroxene bands. Modified after Frezzotti and Peccerillo (2007).

Gorman et al., 2006; Thomsen and Schmidt, 2008; Poli et al., 2009). Carbon outgassing is governed by decompression melting of the carbonated mantle at depths below 250–300 km (Dasgupta and Hirschmann, 2007a, and references cited therein). Carbonate-rich melts generated by very low degrees of melting may be widespread in different geodynamic settings and rapidly react with the mantle over short periods of geologic times (i.e., a few million years; Hammouda and Laporte, 2000).

Fluid inclusions in mantle peridotites record CO₂ fluxing from reacting carbonate melts at high pressure, and suggest significant upper-mantle outgassing over time. Transport of deep carbon towards the exosphere by carbonate melts is a fast process and may account for rapid CO₂ degassing on geologic timescales. Although

this process is yet not fully considered, it may allow for the release of huge amounts of carbon from the mantle into the atmosphere independent of and in addition to volcano degassing. If only 0.1 wt.% of carbonatitic melt present in the upper mantle is out-gassed, mass balance predicts that approximately 1.35 Mt of CO₂ (equal to 0.4 Mt carbon) could be potentially released from each cubic kilometer of metasomatized mantle. Recently, Dasgupta et al. (2006) proposed variable global fluxes of mantle CO₂ between 120 and 3400 Mt/yr from upwelling mantle along the mid-ocean ridge. On the regional scale, a conservative CO₂ flux of about 70 Mt/yr from carbonate-rich melt outgassing was proposed by Frezzotti et al. (2009) in the lithosphere–asthenosphere beneath the western Mediterranean region, which largely exceeds the yearly CO₂ emissions from Italian volcanoes. Although these petrological estimates of deep CO₂ fluxes are huge, not all mantle CO₂ would be able to reach the Earth's surface, since a still unconstrained part may remain in the mantle. In this last case, CO₂-rich fluids could spread throughout the lithosphere, accumulating close to the Moho, and inducing granulite-facies metamorphism of the lower crust in continental settings during discrete episodes of high- to ultrahigh-*T* granulite metamorphism.

8. Concluding remarks

The natural record of fluid phases in the upper mantle preserved in fluid inclusions indicates that high density to super-dense CO₂-rich fluids (\pm brines) are stable in the shallow part of the lithosphere (<100 km) while alkali-carbonate (silicate) melts are stable at greater pressures. Dominant solutes in aqueous mantle fluids are chlorides, silica and alkalis.

The characteristics of many carbonates contained within inclusions suggest that they are remnants of solid or melt phases left behind from metasomatic reactions. Carbonate melts generated in the asthenospheric mantle may react with mantle minerals to trigger release of CO₂-rich fluid fluxes, which may contain a brine component.

Carbonate-rich hydrous fluids or melts are important metasomatic agents for element and volatile transport to the lithospheric mantle. Any model of the mantle must take into account the major effects that they have on lithosphere composition and physical properties. Fluxes of mantle-derived CO₂ (\pm brines) generated from decomposition of carbonate-rich phases may eventually reach upper crustal levels, including the atmosphere.

Acknowledgments

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