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### Fluid inclusions in mantle xenoliths

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#### Abstract

Fluid inclusions in olivine and pyroxene in mantle-derived ultramafic xenoliths in volcanic rocks contain abundant  $CO_{2}$ -rich fluid inclusions, as well as inclusions of silicate glass, solidified metal sulphide melt and carbonates. Such inclusions represent accidentally trapped samples of fluid- and melt phases present in the upper mantle, and are as such of unique importance for the understanding of mineral-fluid-melt interaction processes in the mantle. Minor volatile species in  $CO_2$ -rich fluid inclusions include  $N_2$ , CO, SO<sub>2</sub>, H<sub>2</sub>O and noble gases. In some xenoliths sampled from hydrated mantle-wedges above active subduction zones, water may actually be a dominant fluid species. The distribution of minor volatile species in inclusion fluids can provide information on the oxidation state of the upper mantle, on mantle degassing processes and on recycling of subducted material to the mantle. Melt inclusions in ultramafic xenoliths give information on silicate-sulphide-carbonatite immiscibility relationships within the upper mantle. Recent melt-inclusion studies have indicated that highly silicic melts can coexist with mantle peridotite mineral assemblages. Although trapping-pressures up to 1.4 GPa can be derived from fluid inclusion data, few CO<sub>2</sub>-rich fluid inclusions preserve a density representing their initial trapping in the upper mantle, because of leakage or stretching during transport to the surface. However, the distribution of fluid density in populations of modified inclusions may preserve information on volcanic plumbing systems not easily available from their host minerals. As fluid and melt inclusions are integral parts of the phase assemblages of their host xenoliths, and thus of the upper mantle itself, the authors of this review strongly recommend that their study is included in any research project relating to mantle xenoliths. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Upper mantle; Fluid inclusions; Carbon dioxide; Silicate melts

#### 1. Introduction

The study of fluid inclusions in mantle xenoliths was initiated by Roedder (1965), in a paper which

ranks among the classics of fluid petrology. From microscopic observation, chemical analysis and microthermometry on fluid inclusions in megacrysts and ultramafic xenoliths in mantle-derived mafic magmas from 72 different localities, he could demonstrate the worldwide occurrence of carbon-dioxide fluid inclusions of considerable density in upper mantle minerals. Furhermore, he described, classified and interpreted a wide range of fluid inclusion microstructures observed in such rocks.

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During the decades following the publication of Roedder's paper, a considerable amount of fluid inclusion data have been aquired from ultramafic xenoliths from mantle-derived mafic rocks, using microthermometry and Raman microspectroscopy or fluid extraction methods. Roedder (1994) claimed that ca. 100 localities worldwide had been studied until the early 1990s, and more may have appeared during the last few years. Two separate reviews on the subject were published in the 1980s, the first of which (Roedder, 1984) summarized the observational data available up to ca. 1983: in a subsequent paper he updated this overview to the early 1990s (Roedder, 1994). The other 1980s review, by Pasteris (1987) gave a brief summary of the most important fluid inclusion studies, and discussed in depth the relationship between the fluid compositions observed in inclusions and the volatile regime in the upper mantle, which may not always be simple and straigthforwards.

The present paper does not aim to duplicate any of the earlier reviews of fluid-inclusion studies in mantle xenoliths, but to provide an introduction for new fluid inclusionists to the possibilities and limitations of the field of fluid inclusions in mantle xenoliths. Using published fluid inclusion data from selected suites of mantle xenoliths, this paper will illustrate how in-situ fluid analyses and microthermometry can be used to throw light on the PT history of the host xenolith and on mineral-meltfluid interaction processes in the mantle. Although fluid inclusions in most mantle xenoliths contain pure or nearly pure  $CO_2$ , minor 'exotic' components in the inclusion fluid (e.g., water, nitrogen, methane, carbon monoxide, noble gases) can give important information on fluid regime in the upper mantle, and even hint on processes such as recycling of crustal material. Closely allied to the study of fluid inclusions in mantle xenoliths is the study of melt inclusions, by microscopy, microanalytical methods and high-temperature microthermometry.

The study of diamonds and their inclusions is a separate field, which has contributed significantly to our understanding of the fluid regime of deeper parts of the upper mantle. Such studies require their own techniques, different from the study of fluid and glass inclusions in olivine, pyroxene and other rockforming minerals in upper mantle xenoliths. Inclusion studies in diamonds are not covered by the present paper, but interested readers can be referred to the review of Roedder (1984) and to specialized papers (e.g., Schrauder and Navon, 1993; Wang et al., 1996 and references therein).

The authors claim the right to a partisan view, and confess that this review is firmly based on their conviction that fluid inclusion studies on ultramafic xenoliths provide important constraints on the upper mantle fluid regime and on xenolith petrology.

# 2. The solid phase evidence: what *PT* conditions and mantle regions do the xenoliths come from?

The mineral chemistry of mantle xenoliths brought to the surface in volcanic eruptions may be used to determine the PT conditions at which the xenoliths last equilibrated. The xenoliths recovered in a given area may thus give us important information about the thermal regime and the structure of the underlying mantle.

It is generally believed that mafic magmas are generated below the mantle lithosphere (although their source may involve former lower lithosphere transformed into asthenosphere by heating). Mantle xenoliths brought to the surface by magmas are generally sampled within the lithosphere. There is a clear relationship between the phase assemblages and geothermal gradients defined by different groups of xenoliths, and their tectonic settings (e.g., Nixon and Davies, 1987). The highest geothermal gradients are found for ocean islands (spinel-bearing assemblages) (Fig. 1); the gradients decrease through oceanic plateaux, rifted or faulted intraplate continental areas, back-arc orogenic zones and fold/mobile belts (spinel and/or garnet), and peripheral cratons (garnet), to cratons and cratonized mobile belts (garnet + diamond). Assuming that the lithospheric thickness is defined by the intersection between the geothermal gradient and the relevant peridotite solidus in the area, there is a negative correlation between geothermal gradients and lithospheric thicknesses. Judging from maximum pressures indicated by xenoliths in different areas, geothermometry and geobarometry on mantle xenoliths indicate that the lithosphere beneath the Archean craton of southern Africa is 170-220 km thick, and 130-170 km thick



Fig. 1. Geothermal gradients for different regions based on xenolith mineral thermobarometry (*Malaita, Solomon Islands*: Nixon and Boyd, 1979; *Eastern Australia*: O'Reilly and Griffin, 1985; *NW Spitsbergen*: Amundsen et al., 1987; *Baikal*: Dorofeeva and Lysak, 1989; *Quilin, southeasterns China*: Xu et al., 1996; *Kaapvaal craton and periphery, Africa (heavy full and heavy long-dashed lines, respectively*): Finnerty and Boyd, 1987). For comparison, also shown are points on the geothermal gradients for different ocean islands based on mineral thermometry and CO<sub>2</sub> isochores (*Hierro, Canary Islands*: Hansteen et al., 1991; *Lanzarote, Canary Islands*: Neumann et al., 1995), and CO<sub>2</sub> isochores combined with silicate glass melting temperatures (*Tahaa*: Schiano et al., 1992; *Comores and Tahiti*: Schiano and Clocchiatti, 1994; *Kergulen*: Schiano et al., 1994). Narrow dotted lines indicate conductive geotherms for different heat flow values. Solidus curves (dash-dot lines) are after Wyllie (1981), and the narrow dashed line shows the spinel lherzolite–garnet lherzolite transition.

under the adjacent mobile belts (Finnerty and Boyd, 1987). Somewhat lower thicknesses are implied by the steeper geothermal gradients under the Solomon Islands, NW Spitsbergen, Eastern Australia, and the Baikal and Quilin provinces (Fig. 1). Based on mineral geothermometry and  $CO_2$  isochores, Hansteen et

al. (1991) and Neumann et al. (1995) found the lithospheric thickness under Hierro and Lanzarote (Canary Islands) to be  $\geq 45$  and  $\geq 27$  km, respectively. Very thin lithospheres are also indicated by data from Schiano et al. (1992, 1994, 1995) for other ocean islands (Fig. 1).

# **3.** Distribution and textural characteristics of fluid and melt inclusions in mantle xenoliths

A mantle xenolith is a metamorphic rock, and any fluid contained in inclusions in its minerals is a remnant of a fluid phase which was present at some stage of its history from its initial residence in the upper mantle to its ejection at the surface of the earth. The classical criteria for distinguishing between 'primary', 'pseudosecondary' or 'secondary' fluid inclusions are hard to apply to mantle xenoliths, as these were originally developed for host minerals in igneous rocks and hydrothermal veins (e.g., Roedder, 1984). In a mantle xenolith, as in most other metamorphic rocks, fluid inclusions only rarely occur isolated or in well-defined clusters: the vast majority of inclusions are generally situated along healed fracture trails. This does not, however, necessarily imply that such inclusions are 'secondary' with respect to the metamorphic equilibration of the xenolith minerals within the upper mantle. To characterize the relationship between different groups or generations of fluid inclusions and their host mineral, it is usually necessary to work out local trapping sequences from careful microscopic observation of cross-cutting relationships between trails, as is commonly done in the study of crustal metamorphic rocks (e.g., Touret, 1987, 2001). Microthermometric measurements which have been accumulated without proper textural control are, in most cases, much less valuable and more difficult to interpret than measurements which can be related to well-defined trapping sequences.

Figs. 2–4 show typical illustrations of fluid inclusion textures observed in mantle xenoliths. None of the inclusions shown represent unambiguous 'primary' inclusions according to the textural criteria of Roedder (1984), but randomly scattered or isolated fluid inclusions (Figs. 2a, and 3b,d) were most likely trapped during growth of their host crystal. Secondary inclusions as shown in Figs. 2b and 3a,c were clearly trapped after initial growth of the host crystal, but still while the host mineral resided in the upper mantle.

In most mantle xenoliths,  $CO_2$  fluid inclusions are the only or the dominant type of inclusions observed. Other phases which may be recognized by microscopic observation (using high magnification



Fig. 2. Carbon dioxide fluid inclusions in mantle xenoliths. Length of scale bars: 0.1 mm. (a) Randomly scattered fluid inclusions in olivine in sample GN-23, Gnotuk maar, Victoria, Australia (Griffin et al., 1984; Andersen et al., 1984). These inclusions are not bound to any healed fracture trail, and may have been trapped at the time of growth of the host crystal (i.e. primary inclusions). (b) Trailbound, secondary fluid inclusions in olivine in sample BM-166, Bullenmerri maar, Victoria, Australia (Griffin et al., 1984; Andersen et al., 1984). These fluid inclusions were trapped by healing of a fracture in the host crystal (i.e. secondary inclusions). Notice trails of minute inclusions radiating out from some of the larger inclusions in the trail. These have formed by decrepitation of the original inclusion (see also Fig. 4).

and strongly convergent light) include silicate glass (Fig. 3c), sulphides or solidified sulphide melts (Fig. 3b) and accidentally trapped solids such as spinel (Fig. 3a) or even carbonate (Fig. 3d).

Most fluid inclusions in mantle xenoliths have stretched or decrepitated on their way to the surface



Fig. 3. Evidence of heterogeneous trapping of  $CO_2$  fluid with melts or solids. Length of scale bars: 0.1 mm. (a) Trail with nitrogen fluid inclusions and accidentally trapped solids, Sample LA1–6, Lanzarote, Canary Islands (Andersen et al., 1995). The inclusion indicated by an arrow consists of a nitrogen fluid inclusion attached to a minute spinel platelet. (b) Carbon dioxide fluid inclusions and sulphide melt inclusions in pyroxenite from San Carlos, AZ, USA (Andersen et al., 1987). Carbon dioxide inclusions are in part randomly scattered, and in part trailbound. Sulphide melt inclusions are randomly scattered, and on a meoscopic scale, follow zonation patterns in the host crystal, suggesting that they are truly primary in origin. The inclusion indicated by an arrow consists of a  $CO_2$  inclusion attached to the surface of a solidified sphere of sulphide melt, suggesting heterogeneous trapping of sulphide melt and carbonic fluid. Late, secondary trails with small  $CO_2$  inclusions radiate from some of the primary  $CO_2$  inclusions; these have been formed by decrepitation of the earlier fluid inclusions during ascent. (c) Silicate glass inclusions with  $CO_2$  vapour bubbles in olivine from sample LA6–7, Lanzarote, Canary Islands (Neumann et al., 1995). All inclusions in this frame are trailbound, secondary inclusions. (d) Isolated  $CO_2$  fluid inclusion (primary?) with an attached calcite crystal, sample BM-166 from Bullenmerri maar, Victoria, Australia (Andersen et al., 1984). The calcite was most probably trapped as a solid inclusion together with the fluid. For another mode of occurrence of calcite in fluid inclusions from SE Australia, see Fig. 6.

(see below). Textures which typically form in these processes are illustrated in Fig. 4. Examples of late secondary inclusion trails formed by decrepitation during ascent can also be seen in Fig. 3b.

Silicate glass, ranging in composition from basaltic to silicic, is commonly found as inclusions

and as interstitial glass pockets in upper mantle xenoliths (e.g., Edgar et al., 1989; Zinngrebe and Foley, 1995; Neumann and Wulff-Pedersen, 1997). Host xenoliths for silicic glasses (60–72 wt.% SiO<sub>2</sub>) include anhydrous and hydrous spinel-bearing harzburgites, lherzolites and dunites from continen-



Fig. 4. Decrepitation and stretching textures in mantle xenoliths. Length of scale bars: 0.1 mm. (a) Healed decrepitation fractures radiating from a large  $CO_2$  inclusion, sample BM-166, Bullenmerri maar, Victoria, Australia (Andersen et al., 1984). (b) Halo with nearly concentric, arcuate fluid inclusions which have formed by healing of a decrepitation fracture around a  $CO_2$  fluid inclusion in olivine, sample LA2–7, Lanzarote, Canary Islands (Neumann et al., 1995). Similar circular structures have been argued to form by implosion due to internal underpressure (e.g. Touret, 1992), but this is extremely unlikely in the present case, as the host xenolith has gone through nearly isothermal decompression from mantle conditions to the surface.

tal, oceanic, and island-arc tectonic settings (e.g., Frey and Green, 1974; Francis, 1976, 1987; Jones et al., 1983; Siena et al., 1991; Ionov et al., 1994; Schiano et al., 1992, 1994, 1995; Schiano and Clocchiatti, 1994; Neumann et al., 1995; Zinngrebe and Foley, 1995; Wulff-Pedersen et al., 1996; Neumann and Wulff-Pedersen, 1997). Silicic glass inclusions typically form secondary inclusion trails in porphyroclasts, and primary inclusions in neoblasts. Some inclusion contain only glass, in others silicic glass coexist with  $CO_2 \pm$  daughter minerals. In mantle xenoliths from Batan, Philippine arc, Schiano et al. (1995) found many primary inclusions in neoblasts to consist of silicate glass + H<sub>2</sub>O (vap + liq)  $\pm$ hydrous daughter minerals (plogopite, amphibole) or silicate glass + sulphide; the silicate glass inclusions homogenized at ca. 920°C.

#### 4. The xenolith-fluid inclusion evidence: composition and density

#### 4.1. Carbon dioxide

As observed by Roedder (1965), fluid inclusions in mantle xenoliths are generally dominated by  $CO_2$ , most studies published so far claim that the inclusion fluid is  $CO_2$  without any other detectable fluid species. The properties of 'pure'  $CO_2$  inclusions should therefore be examined before introducing the other, 'exotic' volatile species which have been observed in some studies.

Carbon dioxide inclusions are conveniently characterized by microthermometry (e.g., Roedder, 1984). In the present reivew, the phase transition terminology for carbonic fluid inclusions by Kerkhof (1988) is used (see also Kerkhof and Thiery, 2001). Pure carbon dioxide inclusions show a special type of H3 microthermometric behaviour (Kerkhof, 1988), in which the initial melting temperature of solid  $CO_{2}$  $(T_i)$  coinceedes with its final melting temperature  $(T_{\rm m})$ ; on heating an inclusion above  $T_{\rm m}$ , a two-phase gas + liquid phase assemblage changes to one phase (liquid, vapour or supercritical fluid) at the homogenization temperature  $(T_{\rm h})$ . Components other than CO<sub>2</sub> cause lowering of  $T_i$  and  $T_m$ ; as  $T_i < T_m$  in multicomponent fluid inclusions, vapour and solid CO<sub>2</sub> coexist over a certain temperature range in such inclusions (the melting interval). Some of the most important contaminants may be detected by in-situ analytical methods such as Raman microspectroscopy (Burke, 2001). For a one-component fluid, the homogenization temperature is a univariant function of molar volume (V,  $cm^3/mol$ ) or density (d,  $g/cm^3$ ), which are related by the expression V =M/d, where M is the molar mass. Fig. 5 summarizes the distribution of fluid inclusion densities (molar volumes) observed for pure  $CO_2$  inclusions in 28 selected studies of mantle xenoliths published since 1978. Sources of data used in the compilation are given in Table 1. The data come from different tectonic settings, including oceanic islands (Hawaii, Canary Islands, Polynesia, Indian Ocean), convergent plate margins (Etna, Simcoe) and intra-continental settings (localities in North and South America, Australia, Asia, West and Central Europe).

For each entry in Fig. 5, the following information is included: (i) the maximum fluid inclusion density reported in the origial study; (ii) the most frequent density, represented by the peak of the  $T_h$ histogram (or, in the case of complex histograms, from the most prominent peak); (iii) other, high frequency densities (subordinate histogram peaks or densities cited by the authors); and (iv) the lowest ^

Homogenization to vapour



Fig. 5. The distribution of density (molar volume) in fluid inclusions reported in 28 papers on fluid inclusions in mantle xenoliths published since 1978. Sources of data are given in Table 1. Explanation of symbols: See inset.

density reported (reflecting the highest  $T_h^L$  or any  $T_h^V$  reported in the original study). It should be noted that the low-density cutoff value is not neccessarily a real minimum density limit for the fluid inclusions in a xenolith, as homogenization to vapour in low-density inclusions is notoriously difficult to measure. Such low-density inclusions are also of subordinate interest for most students of mantle xenoliths. The densities shown in Fig. 5 are either values given in the original study, or they have been calculated from

 $T_{\rm h}$  values, using data on the two-phase curve of CO<sub>2</sub> from Angus et al. (1976).

Common to most suites of xenolihs studied are wide ranges of CO<sub>2</sub> density, which in some cases extend from the triple point density of  $CO_2$  (1.18  $g/cm^3$ ) to less than its critical density (0.47  $g/cm^3$ ). Despite of this, Fig. 5 suggests some regional trends in the distribution of fluid inclusion densities: Although fluid inclusions with moderate densities ( < $0.8 \text{ g/cm}^3$ ) are abundant in xenoliths from all localities from Hawaii, several suites of xenoliths from Oahu (Koolau, Salt Lake Crater) have reported fluid inclusions with densities of 1.18 g/cm<sup>3</sup> ( $T_{\rm h} =$  $-56.6^{\circ}$ C) or even 'superdense' fluid inclusions with metastable homogenization to the liquid at  $T_{\rm hm}$  < -56.6 (Murck et al., 1978; De Vivo et al., 1988; Villa et al., 1991: Frezzotti et al., 1991a). Outside of Hawaii, such high maximum densities have only been reported from some continental settings (SE Australia, Andersen et al., 1984, 1987). The largest set of data from a single province in Fig. 5 comes from the Canary Islands (Hansteen et al., 1991, 1998; Frezzotti et al., 1994; Neumann et al, 1995;

Table 1 Sources of homogenization temperatures/fluid inclusion densities used in Fig. 5

Ref. no. in Fig. 5	Source of data
1	Roedder (1983)
2	Murck et al. (1978)
3	Frezzotti et al. (1991b, 1992)
4	Villa et al. (1991)
5	De Vivo et al. (1988)
6	Hansteen et al. (1998)
7	Hansteen et al. (1991)
8	Frezzotti et al. (1994)
9	Ertan and Leeman
	(1994, 1996a,b, 1999)
10	Andersen et al. (1987)
11	Bergman and Dubessy (1984)
12	Frezzotti et al. (1991a)
13	Szabo and Bodnar (1992a,b),
	Huraiova et al. (1991)
14	Török and De Vivo (1995)
15	Andersen et al. (1984, 1987)
16	Varela et al. (1995, 1996)
17	Neumann et al. (1995)
18	Schiano and Clocchiatti (1994)
19	Schiano et al. (1994)
20	Schiano et al. (1992)

Schiano and Clocchiatti, 1994), where individual islands show different ranges of densities. The highest maximum densities are observed in Hierro and Gran Canaria, the lowest in La Palma and Gomera. In xenolith suites from individual islands, there are also systematic variations of maximum density observed between different petrographic groups of xenoliths, with cumulates and gabbroic xenoliths showing a clear tendency towards low maximum densities. Several xenolith suites from the Western USA show maximum  $CO_2$  densities between 0.99 and 1.07 g/cm<sup>3</sup> and peak-frequencies close to the maximum densities. Similar maximum densities are seen in other continental areas, in Eurasia reaching a maximum of 1.14 g/cm<sup>3</sup> (Fig. 5).

#### 4.2. Other volatile species

Although most fluid inclusions in mantle xenoliths contain  $CO_2$  with other species in quantities less than can be detected by microthermometric observations or by the analytial methods commonly used, a number of studies have recorded or suspected other volatile species in fluid inclusions from mantle xenoliths.

Minor and trace components in fluid inclusions can either be detected in-situ in individual inclusions by Raman microprobe (Burke, 2001), or determined by mass spectrometry on bulk fluid extracted by crushing or decrepitation (Villa, 2001). The former method is non-destructive and easy to combine with microthermometry, but has the disadvantage of a relatively high detection limit (on the order of 0.x mol% for most species of interest), and excludes potentially important components such as water and the noble gases. Mass spectrometry is a far more sensitive method, but can only give bulk fluid compositions, which cannot easily be related to microthermometric observations. Also, reaction between molecular carbonic species in the extracted fluid and fragments of the host mineral is possible, especially if temperature-induced decrepitation is used as extraction method, this could generate molecular carbonic species which were not initially present in the inclusion fluid. However, hydrocarbons have also been observed in inclusion fluids extracted by crushing at room temperature, which should not cause synthesis of such molecules (O'Reilly et al., 1990). This is obviously a field for further study.

#### 4.2.1. Water

Water is an elusive component in fluid inclusions in mantle xenoliths, firstly because it can be difficult to observe, and secondly because it may react with the host mineral while in the mantle or during eruption. It is usually claimed that 10 vol.% of water can pass undetected by visual observation, as it will wet the walls of an inclusion cavity (e.g., Roedder, 1984). However, water in volume-percent amounts is likely to be revealed by the formation of a solid clathratehydrate at low T and its subsequent melting at  $T \leq +10^{\circ}$ C. The CO<sub>2</sub>-clathrate is generally quite easy to observe in CO<sub>2</sub>-dominated fluid inclusions, unlike in water-rich inclusions, where there is virtually no difference in optical relief between solid clathrate and liquid water. Olivine and pyroxene differ from quartz as a host phase for fluid inclusions, in that local hydration reactions (forming amphibole or sheet silicates) may deplete the fluid in water in-situ in a fluid inclusion.

CO<sub>2</sub>-H<sub>2</sub>O inclusions with major amounts of water have been observed in xenoliths from Ichinomegata (also known as Itinome-gata), Japan (Roedder, 1965; Trial et al., 1984), and inclusions containing  $H_2O$  (vap + liq) and silicate glass + hydrous daughter minerals (plogopite, amphibole) were described from Batan, Philippine arc (Schiano et al., 1995). Both of these occurrences are situated above active subduction zones, and the Ichinomegata xenoliths differ from most other mantle xenoliths in being carried by andesite as well as basalt (e.g., Sakuyama and Koyaguchi, 1984). Water-bearing fluid inclusions are also recorded from ultramafic nodules in plinean ejecta from Vesuvius. Italy, but these nodules formed by accumulation in a subvolcanic magma chamber (Belkin and De Vivo, 1993), and are thus not mantle xenoliths.

Andersen et al. (1984) reported indirect evidence of the previous existence of  $H_2O$  and  $Cl^-$  as components in fluid inclusions in olivine and pyroxene in xenoliths from the Bullenmerri and Gnotuk maars in SE Australia. In these xenoliths,  $CO_2$  inclusions are extremely abundant; optical microscopy and SEM imaging of opened inclusions show that carbonates and chlorine-bearing amphibole have formed as solid products of reaction between a complex initial fluid and the host pyroxene or olivine (Fig. 6). Some of the xenoliths from these localities are miarolitic, with amphibole and garnet protruding into interstitial cavities, demonstrating that the water-bearing fluid was an integral part of the mantle high-pressure phase assemblage, and not due to late-stage interaction with crustal, aqueous fluids. While still in the mantle, water was removed from the inclusion fluid by reaction between fluid and inclusion walls. The present-day 'pure'  $CO_2$  in these inclusions is thus a residual fluid. Based on mineral reactions of the type:

Anhydrous host mineral + H<sub>2</sub>O + CO<sub>2</sub>

= amphibole + carbonate

whose stoichiometry could be deduced from SEM observation and semiquantitative EDS analyses of minerals in opened inclusion cavities, it was possible to derive an upper limit of  $X_{\rm H_2O}$  of ca. 15 mol%. Higher water contents would not be compatible with the maximum densities observed in residual CO<sub>2</sub> inclusions (d = 1.18 g/cm<sup>3</sup>). Andersen et al. (1984)

extended their argument to suggest the former presence of minor amounts of CO, which as also removed by reaction with the inclusion walls, but evidence for this must be regarded as much weaker than the evidence for the former presence of water in these xenoliths.

#### 4.2.2. Methane

Methane (and higher hydrocarbons) are stable in the COH system at reducing conditions and quite elevated temperatures (Huizenga, 2001), and may be of importance in the mantle (Pasteris, 1987). The possibility of transport of major amounts of hydrocarbons from the mantle along deep fractures (such as are formed in meteorite impact structures) to crustal traps was proposed by Gold (1979), and would, if true, have major implications for the Earth's hydrocarbon supply and thus for the global economy. Drilling for abiogenic hydrocarbons in a major meteorite impact structure in an intracontinental setting has been attempted without success (e.g., Kerr, 1990; Roedder, 1994). Furthermore, no findings of CH<sub>4</sub> in



Fig. 6. Randomly scattered (primary?)  $CO_2$  inclusions in clinopyroxene in sample GN-23, Gnotuk maar, Victoria, Australia (Andersen et al., 1984). The inserted frame to the upper left show the central group of inclusions under crossed polarizers (same magnification as the main frame), the lower right inset is a closeup of the largest inclusion in the group. The strongly birefringent, minute grain attached to the inclusion cavity wall is a calcite crystal having formed in-situ by reaction between the host mineral and a complex  $CO_2$ –H<sub>2</sub>O–(CO) primary inclusion fluid.

detectable amounts in mantle xenoliths have been reported, which may be due to post-trapping processes (Pasteris, 1987), or simply to its absence from those parts of the mantle which are sampled by mafic magmas.

#### 4.2.3. Nitrogen

 $N_2$  is the only 'exotic' species apart from water which has been shown to occur in major amounts in inclusion fluids in mantle xenoliths. Pasteris (1987) referred to trace amounts of nitrogen in xenolith inclusions, without presenting data or references to original studies. Huraiova et al. (1991) reported the first direct determination of minor  $N_2$ , amounting to 0.14–0.38 mol% of a CO<sub>2</sub>-dominated carbonic fluid in xenoliths and megacrysts from Filàkovské Sovàce, Slovakia. The first, and so far only, mantle xenoliths with pure nitrogen inclusions and CO<sub>2</sub>– $N_2$  mixtures with major  $N_2$  were reported from spinel dunite xenoliths from Lanzarote, Canary Islands (Andersen et al., 1995). In these xenoliths, there is a continuous range of composition from 0 to 100 mol%  $N_2$ .

#### 4.2.4. Noble gases

Noble gases in fluid inclusions in mantle xenoliths are of great potential interest for the understanding of the volatile budget and evolution of the mantle through time, as the isotopic composition of He and Ar can give unique information on the mantle degassing history. A high <sup>3</sup>He signature is indicative of origin from a primitive, undegassed and probably deep mantle reservoir (e.g., Kurz, 1991). Considerable research effort has therefore been made in this field, and several authors report noble gas isotope data from mantle xenoliths (e.g., Porcelli et al., 1986; Villa et al., 1991; Rocholl et al., 1996; Matsumoto et al., 1996, 1998). The presence of even very minor amounts of a noble gas with low  $T_t$  and  $T_{\rm c}$  (in particular He) can be expected to have significant influence on the melting and homogenization behaviour of  $CO_2$ , but the phase systematics of CO<sub>2</sub>-He-Ne-Ar system(s) are still largely unknown. Villa et al. (1991) related He detected by mass spectrometry on extracted bulk inclusion fluids to low  $T_{\rm m}$ -values observed in individual CO<sub>2</sub> inclusions in xenoliths from Oahu, Hawaii. Trace amounts of noble gases undeniably occur in those fluid inclusions, but the connection between these and a melting-point depression of solid  $CO_2$  of several degrees may be questionable. Responsibility for depressing  $T_{\rm m}$  was assigned to noble gases by Villa et al. (1991) because no Raman-active molecular species other than  $CO_2$  could be detected in the fluid inclusions. Meanwhile, nitrogen has been recorded as a major component in some mantle fluids, and and  $SO_2$  in others (see Section 4.2.6). The question may be asked which would have the stronger influence on  $T_i$ ,  $T_{\rm m}$  and  $T_{\rm h}$ ; noble gases in the 10–100 ppm concentration range, or  $\leq 0.x$  mol% N<sub>2</sub> or SO<sub>2</sub> (Frezzotti et al., 1992)?

#### 4.2.5. Carbon monoxide

At the *PT* conditions of the upper mantle, CO would be expected to be a significant component in COH-fluids in equilibrium with mantle minerals (Andersen et al., 1984, Pasteris, 1987). However, only one paper has reported definite evidence of major CO, in an amphibole vein in a wherlite xeno-lith from Lunar Crater, Nevada, USA (Bergman and Dubessy, 1984). CO was detected by Raman micro-probe, and amounts to 8.5–12 mol%. The only other published direct observation of minor CO was made by Huraiova et al. (1991), in fluid inclusions from Southern Slovakia, which also contain minor nitrogen.

#### 4.2.6. Sulphur species and metal sulphide melt

Murck et al. (1978) reported  $CO_2$  fluid inclusions in xenoliths from Hualalai, Hawaii, which have  $T_{\rm m}$ < -56.6 but  $T_{\rm h} > +31.4$ °C. These observations suggest the presence of minor amounts of volatile species with lower triple-point temperature  $(T_t)$  but higher critical temperature  $(T_c)$  than CO<sub>2</sub> in the inclusion fluid. Few such species are available, and  $H_2S$  ( $T_t = -85.5^{\circ}C$ ,  $T_c = 100.4^{\circ}C$ ) and  $SO_2$  ( $T_t =$  $-72.7^{\circ}$ C,  $T_{c} = 157.8^{\circ}$ C) were suggested as likely candidates. Although these species are quite likely contaminants, it should be pointed out that the study was made before the introducition of the Raman microprobe, and that the contaminant therefore could only be identified from the microthermometric behaviour of the inclusion fluid, which in case of COHN fluids has proven inconclusive if unsupported by analytical data (e.g., Kerkhof, 1988). A reexamination of the material of Murck et al. (1978) with a Raman microprobe is suggested.

In spinel lherzolite and harzburgite xenoliths from Tenerife, the presence of  $1-2 \mod 80_2$  in highdensity, carbonate-bearing CO<sub>2</sub>-rich inclusions have been verified by Raman analyses (M.L. Frezzotti, personal communication, 1999). These early CO<sub>2</sub>-rich inclusions occur in clusters or form randomly orientated trails in orthopyroxene.

The coexistence of sulphide melt inclusions and high-density  $CO_2$  in some pyroxenite xenoliths definitely indicate that sulphur-bearing species are important in the upper mantle (Andersen et al., 1987; Kozlowski and Metz, 1990; Guo et al., 1999). Textural evidence combined with SEM imaging of opened inclusions demonstrated that sulphide inclusions in a pyroxenite xenolith from Kilbourne Hole, New Mexico (USA) were formed by homogeneous trapping of sulphide melt containing up to 10 wt.%  $CO_2$ ;  $CO_2$ exsolved as a separate fluid phase after trapping, leaving a  $CO_2$  bubble within a (now solidified) outer shell of sulphide melt (Andersen et al., 1987).

Spinel harzburgite, lherzolite and dunite xenoliths from the Canary Islands contain globular sulphide inclusions, present as scattered (primary?) inclusions as well as secondary inclusion trails in porphyroclasts, and as primary inclusions in neoblasts (e.g., Hansteen et al., 1991; Neumann, unpublished data). Sulphides also coexist with silicate glass and other phases in polyphase inclusions (e.g., Hansteen et al., 1991; Schiano et al., 1992, 1994; Wulff-Pedersen et al., 1996), suggesting the presence of a former sulphur-rich silicate melt in the mantle.

The inclusion assemblage of neoblasts in xenoliths from Batan, Philippine arc described by Schiano et al. (1995) is of particular interest, as it comprises sulphide droplets in addition to aqueous fluid and hydrous silicate glass, indicating the former presence of a water- and sulphide bearing silicate melt, which was saturated in  $H_2O$  and sulphide throughout its crystallization.

#### 4.2.7. Carbonate and carbonatite inclusions

The modal and chemical compositions of many mantle xenolith suites have been explained as the result of metasomatism by carbonatitic fluids (e.g. Green and Wallace, 1988, 1989; Yaxley et al., 1991; Green et al., 1992; Hauri et al., 1993; Ionov et al., 1993). The finding of inclusions in mantle rocks

which may represent trapped carbonatite melts are therefore very important. Such inclusions are not frequent, but some occurrences have been described. In mantle xenoliths from Ouarternary volcanoes in NW Spitsbergen carbonates occur as primary granular aggregates, as quenched melts, and as patches and veins of quenched carbonate and silicate melts (Amundsen, 1987, Amundsen et al., 1987; Ionov et al., 1993). The carbonate is commonly dolomite, in some cases accompanied by magnesite. In some samples composite fluid-carbonate inclusions are common in Al-Na-rich silicate glass (53-58 wt.%  $SiO_2$ ). Amundsen (1987) proposed that the silicate and carbonate glasses formed by liquid immiscibility from a silicic carbonatite melt, whereas Ionov et al. (1993) concluded that the carbonate melts formed by partial melting of carbonates formed previously by reactions between peridotite and carbonatite melt. and that the Na-Al-rich silicate glass formed by local partial melting of silicate minerals in the peridotite. Mantle xenoliths from the Kerguelen Islands (southern Indian Ocean) contain secondary inclusion trails (hosted by olivine, clinopyroxene and orthopyroxene) of silicate glass, carbonate-rich inclusions and  $CO_2$  fluid inclusions; all three types may occur along the same trail (Schiano et al., 1994). Based on their textural relationships Schiano et al. (1994) interpreted the silicate and carbonatite melt to have formed by immiscible separation of a single melt due to a decrease in pressure and temperature. Ti-Fe-rich cumulate xenoliths from Gomera, Canary Islands, exhibit inclusions in olivine containing devitrified ultramafic silicate glass + carbonate (Frezzotti et al., 1994). Kogarko et al. (1995) found carbonate + interstitial silicate glass (ca. 64 wt.% SiO<sub>2</sub>, mildly silica-oversaturated) + sulphide globules in Ti-Ferich wehrlitic alteration zones in a harzburgite xenolith  $(Fo_{91})$  from the Montana Clara Island (Canary Islands). Also these associations of carbonatitic and silicic glasses were interpreted as the results of immiscible separation from a silica-bearing carbonatite melt at mantle pressures (Frezzotti et al., 1994; Kogarko et al., 1995).

It is worth noticing that so far all reported observations in fluid inclusions of material which may be interpreted as representing carbonatitic melts are associated with silicate glass, although of different compositions. It thus seems very likely that carbonatitic melts in the mantle result from immiscible separation from silica-bearing carbonatite melts.

# 5. Fluid density, trapping conditions and xenolith transport

# 5.1. $CO_2$ -densities and processes after inclusion trapping

Clearly, not all of the fluid inclusion densities observed in xenoliths can reflect trapping processes in the mantle: in fact, a vast majority of the fluid inclusions measured may have suffered severe posttrapping modification during ascent to the surface. A fluid inclusion in a pyroxene or olivine in-situ in the upper mantle will have a density in equilibrium with the ambient PT conditions, defined by the intersection of the geotherm with the appropriate isochore. When picked up as an accidental xenolith by a rising, hotter magma, fluid inclusions in xenolith minerals will experience both an initial temperature increase and a drop of external pressure (Fig. 7a), as the transport to the surface is a near-isothermal decompression process. This leads to development of a rapidly increasing internal overpressure ( $\Delta P > 0$ ) within the fluid inclusion. In response to the changing pressure and temperature, most fluid inclusions will stretch (i.e. increase their physical volume without the loss of material) or decrepitate (leak material to the surroundings), both of which processes reduce the density of the inclusion fluid and readjust its internal pressure to the confining pressure at the point along the magmatic conduit where the process takes place (Fig. 7c).

At 1000°C and surface pressure, a pure  $CO_2$ inclusion homogenizing to liquid at -56.6°C (corresponding to maximum densities observed in e.g., Hawaii and SE Australia, Fig. 5) has an internal overpressure of ca. 1.37 GPa (according to the equation of state of Holloway, 1977, 1981). Experimental evidence suggests that fluid inclusions tend to decrepitate at internal overpressures of only a few hundred MPa (Bodnar et al., 1989). Nevertheless, the presence of dense  $CO_2$  inclusions in xenoliths show that some fluid inclusions are able to escape reequilibration, even at such extreme internal overpressures. However, it is not possible to *exclude* the possibility of leakage or decrepitation in any fluid inclusion in mantle xenoliths, not even those homogenizing at or below the triple point of  $CO_2$ . As no processes likely to *increase* the density of the inclusion fluid (e.g., implotion, which may occur in systems suffering isobaric cooling, Touret, 1992) are likely to affect a fluid inclusion in a xenolith carried by an ascending magma column, *it can safely be assumed that the maximum density observed in a population of fluid inclusions represent a minimum limit for the trapping pressure of that inclusion population, but not necessarily its true trapping pressure.* 

#### 5.2. Limits for fluid inclusion trapping pressure

To define limits for the minimum trapping pressures of fluid inclusions in mantle xenoliths, isochores have been calculated for selected minimum homogenization temperatures for xenoliths or suites of xenoliths reported in Fig. 5. Isochores have been calculated using the modified Redlich–Kwong equation of state of Holloway (1981), and are presented in Fig. 8, together with examples of geothermal gradients and mantle peridotite solidi.

The highest densities observed in  $CO_2$  inclusions from Hawaii and SE Australia reflect minimum trapping pressures well above 1.4 GPa. The consistent group of maximum densities observed in the Western United States, including both the subduction-zone related Simcoe xenoliths and the intra-continental occurrences in Nevada and Arizona, correspond to trapping between 0.8 and 1.0 GPa, whereas xenoliths from intracontinental localities in Europe and Asia show minimum trapping pressures up to ca. 1.2 GPa. The Canary Islands present a wide range of minimum trapping pressures, from ca. 1.0 GPa in the earliest Hierro inclusions, to less than 0.3 GPa in Gomera. Also, in Hierro and La Palma, certain xenolith types or well-defined populations of CO<sub>2</sub> inclusions reflect much lower trapping pressures than the maximum values observed in the same xenolith suites. Other oceanic xenoliths suites (Indian Ocean, Pacific other than Hawaii) show minimum trapping pressures within the range of the Canary Islands (compare densities from Fig. 5 with isochores in Fig. 8).



Fig. 7. Cartoons illustrating two different scenarios for post-trapping modification of fluid inclusions in mantle xenoliths. Initial trapping of a high-density  $CO_2$  inclusion in pyroxene or olivine of a mantle peridotite takes place at the point of intersection of the relevant isochore (solid line) with the ambient geothermal gradient (dash-dot line). A fragment of this, cooler, part of the upper mantle is picked up as a xenolith by an ascending, hotter magma (grey arrow). In this process, initial heating is combined by rapid decompression during ascent, causing decrepitation/stretching of fluid inclusions. The *PTt* path of a mantle xenolith is shown as a broken line. The corresponding, internal *PTt* paths of fluid inclusions are shown as small, black arrows. (a) Shows a scenario where inclusions are brought to the surface by continuous transport in a magma. Decrepitated fluid inclusions cool to low temperature along secondary, low-density isochores, some of which are shown (with black arrows). (b) Shows an alternative scenario, which includes a short episode of ponding in an intermediate magmachamber. (c) The qualitative realationship between internal overpressure of a fluid inclusion and time for the scenarios in a and b. (d) The  $CO_2$  homogenization temperature histograms resulting resulting from the scenarios of xenolith ascent illustrated in a (upper curve) and b (bottom curve).

## 5.3. Low-density fluid inclusions and their possible significance

Most fluid inclusion studies on mantle xenoliths show a high frequency of inclusions with elevated  $T_h^L$ , corresponding to densities less than ca. 0.6 g/cm<sup>3</sup>, or of inclusions homogenizing to vapour. Clearly, few if any, of these represent trapping processes in the upper mantle, but must reflect inclusions which have been disturbed by stretching or decrepitation during ascent in the magma column (see review of lattice-scale evidence for such processes by Viti and Frezzotti, 2001), or they contain fluid actually trapped during ascent. Inclusions showing textural evidence of heterogeneous trapping of  $CO_2$  and basaltic glass compositionally indistinguishable from the enclosing lava clearly belong in the latter group.

Distinct low-density peaks in homogenization temperature histograms may be due to an essentially random process of stretching/decrepitation and retrapping of fluid when early inclusions rupture because of internal overpressure (Fig. 7a). However, the apparent systematic overlap of the low-density peaks within some volcanic provinces (see, in particular, the ca. 0.5 g/cm<sup>3</sup> peak observed in La Palma



Fig. 8. Limiting pressure and temperature conditions for fluid inclusion trapping in mantle xenoliths from different provinces. The isochores (thin, solid lines) have been calculated for pure  $CO_2$  with the densities indicated, using the equation of state of Holloway (1981). The boundaries between the garnet-, spinel-, and plagioclase periodtite fields are reproduced from Neumann et al. (1995). Boxes of trapping conditions have been estimated from the data in Fig. 5. Lettered curves: (a) Stable continental geotherm (Wyllie, 1981). (b) Xenolith-defined geotherm for South-East Australia (Griffin et al., 1984). (c) Oceanic plate geotherm and (d) Mid ocean ridge geotherm (both from Wyllie, 1981). (e) Wet peridotite solidus (Olafsson and Eggler, 1983). (f) Dry peridotite solidus (Takahashi and Kushiro, 1983).

and Gomera, Canary Islands, Fig. 5) may be incompatible with random stretching or decrepitation. Frezzotti et al. (1991a) and Hansteen et al. (1998) have suggested that that prominent low-density peaks in  $T_h$ -histograms from xenoliths from Etna and the Canary Islands, respectively, reflect short-time ponding of magma in magma chambers at intermediate depth (Fig 7b). Residence in such magma chambers must necessarily have been short, to prevent dissaggregation or dissolution of the xenoliths and total reequilibration of the silicate mineral systems to new *PT* conditions. As decrepitation and stretching of fluid inclusions are extremely fast processes, compared to recrystallization of solids and exchange of cations between condensed phases, the fluid inclusion assemblage could be able to record such processes not seen by their host minerals. Fig. 7 illustrates two possible scenarios of fluid reequilibration, one a completely random reequilibration process during continuous decompression producing a skewed distribution of low-density fluids (Fig. 7a,d), the other involving a short period of residence at intermediate pressures, which effectively resets the fluid inclusions to the new *PT* conditions, leaving a histogram peak at intermediate homogenization temperatures (Fig. 7b,d).

## 6. Significance of the exotic fluid species in mantle xenoliths

#### 6.1. Carbon monoxide and methane

The reduced carbonic volatile species are related to each other and to  $CO_2$  and water through a number of oxygen- and water-fugacity dependent equilibria (e.g., French, 1966; Huizenga, 2001). In general, elevated temperature and low  $f_{0}$  (oxygen fugacity) would stabilize reduced carbonic species at the expense of  $CO_2$ , in contrast to what is commonly seen in fluid inclusions in upper mantle xenoliths. Readers are referred to the in-depth discussion of this problem by Pasteris (1987). However, loss of water or hydrogen after trapping is unlikely to be a general cause for the lack of species other than CO<sub>2</sub> in fluid inclusions in mantle xenoliths. In cases where such processes do occur, they are likely to leave behind evidence in form of solid reaction products (Andersen et al., 1984). If methane is destabilized by diffusive hydrogen-loss, a graphite coating on the cavity walls should be expected, which can be detected by the Raman microprobe.

#### 6.2. Water

The absence of free water from a vast majority of inclusions in mantle xenoliths does not imply an anhydrous upper mantle: In the regions of the upper mantle sampled as xenoliths in mafic magmas, water may be preferentially partitioned into hydrous minerals such as amphibole or phlogopite. Water may also be removed from trapped fluids by in-situ hydration reactions, as discussed in Section 4.2.1. The two significant occurrences of mantle xenoliths with inclusions containing free water (Ichinomegata, Japan, and Batan, Philippines) represent special, subduction-related settings, where the magmas have sampled a metasomatized mantle wedge, which has been affected by aqueous fluids driven off the downgoing slab (Schiano et al., 1995; Johnson et al., 1996).

#### 6.3. Nitrogen

Despite the enrichment of nitrogen in the atmosphere, biosphere and in sedimentary rocks, the dominant global nitrogen reservoir is the mantle, with an

estimated maximum concentration of ca. 14 ppm (Baur and Wlotzka, 1974). The parts of the upper mantle sampled by mafic magmas may have concentrations lower than the average mantle, as they may have been degassed both early in the Earth's history. and by later magmatic events (e.g., Zhang and Zindler, 1993). The nitrogen occurring as a major fluid species in xenoliths from Lanzarote may in principle have been introduced to the upper mantle domain by metasomatic fluids, draining pristine nitrogen from large volumes of underlying, fertile and non-degassed mantle, or by recycling of biologically bound nitrogen through subduction of sedimentary material. Under favourable physical conditions (elevated water activity, low oxygen fugacity), mineralogically bound ammonium may possibly survive subduction to great depths, to be re-incorporated into volatile-bearing minerals of the mantle peridotite.

The nitrogen budget of the upper mantle may be controlled by the prevailing water activity and oxygen fugacity. Oxidation–devolatilization reactions involving minerals where  $NH_4^+$  substitutes for K<sup>+</sup>, such as

$$\begin{split} & 2\{(NH_4)Mg_3AlSi_3O_{10}(OH)_2\}_{Phl} + Fo + 3/2O_2 \\ & = Sp + 7En + N_2 + 6H_2O \end{split}$$

which involves phlogopite, spinel, olivine and orthopyroxene, and similar reactions with  $NH_4$ -bearing potassium richterite, are likely to control the nitrogen speciation (Andersen et al., 1995).

In the presence of water-bearing fluids, or at conditions where hydrous silicates are stable, nitrogen may generally be partitioned into the solids, explaining the scarcity of  $N_2$  in fluid inclusions in upper mantle xenoliths on a global scale. Nitrogen bound as ammonium in silicate minerals is most efficiently released by lowering the water activity, which can, for example, be caused by introduction of  $CO_2$ -rich fluids from metasomatizing silicate melts. The mantle xenoliths from Lanzarote containing pure  $N_2$  and  $CO_2-N_2$  fluid inclusions are most likely examples of this type of process.

# 7. Glass and glass-fluid inclusions — mantle melts or infiltration during xenolith ascent?

The formation of basaltic melts by partial melting of mantle rocks under different conditions has been demonstrated in a series of experimental studies (e.g., Mysen and Boettcher, 1975; Takahashi and Kushiro, 1983). The origin of silicic glass in mantle xenoliths, and its role in mantle processes in contrast, has been, and is, the subject of vigorous debate. Proposed models include: (i) breakdown of amphibole in response to decompression during transport of the xenoliths to the surface, and heating by the host lava (e.g., Frey and Green, 1974; Francis, 1987: 53-60 wt.% SiO<sub>2</sub>); (ii) immiscible separation of a single melt into coexisting silicic and carbonate melts (Schiano et al., 1994): (iii) small degrees of partial melting of subducted crust followed by percolation of the melts into the overlying depleted mantle wedge in volcanic arcs (Schiano et al., 1995): (iv) infiltration by migrating metasomatic melt phases genetically unrelated to the mantle rock in which they are found (Edgar et al., 1989; Schiano et al., 1992, 1994, 1995: Schiano and Clocchiatti, 1994): (v) reactions between infiltrating basaltic melts and peridotite wall-rock leading to silicic residual melts (Zinngrebe and Foley, 1995; Wulff-Pedersen et al., 1996); (vi) metasomatic reaction between an alkali-carbonatitic melt and mantle minerals (Coltorti et al., 1999); (vii) in situ melting involving breakdown of amphibole + phlogopite (Amundsen et al., 1987); (viii) in situ melting of clinopyroxene + spinel + amphibole (Francis, 1987; Chazot et al., 1996); (ix) disequilibrium in situ melting involving largely clinopyroxene and spinel owing to reaction with migrating fluids (Ionov et al., 1994); and (x) partial melting of peridotite which has previously been metasomatized by carbonatitic melts (Hauri et al., 1993).

There is considerable evidence that silicic melts form at mantle depths, and do not represent processes taking place during transport towards the surface. P-T determinations based on homogenization temperatures of polyphase inclusions combined with microthermometry on CO<sub>2</sub>-inclusions associated with silicic melts indicate trapping at mantle depths (pressures up to 1.25 GPa; Figs. 1 and 8). Recently, experimental investigations have indicated that under upper mantle pressures and temperatures, silicic (56–62 wt.% SiO<sub>2</sub>), aluminous, alkaline melts, typical of silicic glasses found in mantle xenoliths, have near-liquidus mineral assemblages and mineral compositions which indicate equilibrium with a harzburgite residue, both in the presence of a CO<sub>2</sub>–H<sub>2</sub>O fluid and under anhydrous conditions (Baker et al., 1995: Drury and Fitz Gerald, 1996: Draper and Green, 1997). Draper and Green (1997) proposed that silicic, aluminous, alkaline melts may form by low degree partial melting of peridotite enriched in alkalies, volatiles, and other low-melting-temperature components. Equilibrium between silicic melts and peridotite wall-rock is supported by observations which show no indications of reactions between silicic melts and host peridotite minerals, in contrast to the reaction-type contacts between xenoliths and basaltic melts seen in the veined xenoliths, and along the surfaces of unveined xenoliths (Zinngrebe and Foley, 1995: Wulff-Pedersen et al., 1996). It should be noticed that equilibrium, or near-equilibrium, between melt and host peridotite will also be attained by residual, silicic melts which represent the endproducts of reactions between infiltrating basaltic melts and peridotite wall-rocks. Available information thus suggests very low degrees of in situ partial melting, and reactions between infiltrating basaltic melts and mantle peridotite as the most likely modes of formation of silicic melts in the mantle.

#### 8. Concluding remarks

Traditionally, fluid inclusions in mantle xenoliths are regarded as containing essentially pure CO<sub>2</sub>, which may record trapping- or reequilibration pressures, but which are less valuable as indicators of the fluid regime in the upper mantle, or the history of mantle evolution. The advent of new and more sensitive analytical techniques, coupled with a better understanding of the phase properties of fluids and silicate melts have significantly improved this situation: the presence of minor volatile components (water, nitrogen, noble gases) in fluid inclusions gives us insight into processes such as mantle degassing, mantle metasomatism and recycling of sediments. The discovery of silica-rich glass inclusions  $(60-72 \text{ wt.\% SiO}_2)$  in mantle minerals has opened an entirely new field of melt-mineral interaction processes for study. Even when restricted to classical microthermometry of pure CO<sub>2</sub> inclusions, new and exiting perspectives are opening: Are, for example, the very common low-density fluid inclusions just the results of random after-trapping processes, or do they give significant information on volcanic plumbing systems and eruption mechanisms? Much more systematic work is needed to answer this question, which may eventually integrate xenolith petrology into physical volcanology.

The available V-X data on carbonic fluid inclusions in upper mantle xenoliths (Figs. 5 and 8) indicate that fluid inclusions have been trapped or requilibrated within the shallower part of the lithospheric mantle sampled by mantle xenoliths (compare Fig. 8 with Fig. 1). This sets some limitations to the applicability of fluid inclusions as indicators of the fluid regime in the mantle: Little or no information on fluids present in the pressure-range in excess of ca. 1.4 GPa have been obtained by direct observations of carbonic fluid inclusions - beyond this limit, only indirect methods (fluid modelling from mineral equilibria) or the study of inclusions in diamonds are avaiable. However, the part of the lithospheric mantle available for study through fluid and melt inclusions in common ultramafic xenoliths is the domain most likely to give us significant information on processes in the mantle in the geologic past, including crust-mantle interaction, depletion processes, mantle metasomatism and recycling of crustal material through subduction.

Fluid inclusions are present in most mantle xenoliths brought to the surface by volcanic eruptions, in some cases in great abundance. The most important methods required for their study are widely available: a lot can be learned by observation with a good petrographic microscope, and basic V-X data required for petrological interpretation can be obtained on a simple microthermometry stage. More sophisticated analytical techniques include laser-Raman microprobe analysis and mass spectrometry, both of which are becoming increasingly available in research centres specializing in the study of fluid inclusions. A simple method which has proven very fruitful in the study of mantle fluids, but which is not much used in other fields of fluid inclusion research, is SEM imaging of opened inclusions and SEM-EDS analysis.

Our understanding of fluid-melt-mineral interaction in the mantle should be built on information from three independent approaches: (1) experimental studies of melting- and sub-solidus processes in peridotitic systems; (2) petrological and geochemical studies of mantle xenoliths and their minerals, including thermobarometry and thermodynamic modelling of mineral equilibria, and (3) the study of fluid and melt inclusions in minerals in mantle xenoliths. Such fluid and melt inclusions are the only samples of actual mantle melts or fluids available for study. As such, they represent a unique source of data on fluid–rock interaction processes, fluid compositions and, to some extent also the physical properties of fluids in the upper mantle, whose potential importance cannot be overestimated. A careful and systematic investigation of fluid and melt inclusions should be integrated in any serious study of the mineral chemistry and phase equilibria in mantle xenoliths.

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