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Water content and nature of solutes

in shallow-mantle fluids from fluid inclusions

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Abstract

This study discusses new and published data on the composition of fluid inclusions contained in mantle minerals of spinel and garnet peridotite xenoliths, in samples from geodynamically distinct settings (Ethiopian plateau, Hawaii, Canary Islands, and western Mediterranean region). Based on spectroscopic Raman and FTIR analyses we show that, contrary to a commonly held view, fluid inclusions either contain relevant amounts of unsuspected H₂O, or represent a “dehydrated” composition from multicomponent aqueocarbonic fluids. We identify water loss from fluid inclusions through decrepitation, stretching and hydrogen diffusion. We also show that talc, magnesite, chlorides, and sulfates represent common phases in fluid inclusions. Talc and magnesite form through reactions of fluids with the surrounding minerals. Thermodynamic modeling in the MFSHC system of observed reactions between fluid inclusions and surrounding mantle minerals provides the basis for predicting water amounts in shallow-mantle fluids, and suggests X_{H₂O} in the range of 10-50 mole %. Model hydrous fluids are relatively enriched solutions, dominated by Si, Cl, and alkalies, with significant Ca, and S, and low Mg and Fe. This study argues that multicomponent hydrous fluids may be widespread in the shallow mantle, not only in subduction zones but also in intraplate and extensional settings.

Keywords: Mantle petrology, Upper mantle fluid, fluid inclusions, Raman spectroscopy, FT-IR spectroscopy
Introduction

The volatile (e.g., C, O, H and halogens) inventory in the Earth’s upper mantle includes accessory phases, nominally anhydrous minerals (NAMS), along with mobile fluid phases and volatile-rich melts (e.g., Bell et al., 2003; Bolfan-Casanova et al., 2000; Dasgupta and Hirschmann, 2006; Green and Falloon, 1998; Thompson, 1992; Wyllie and Ryabchikov, 2000).

Hydrous fluids are critical to understand the structure and dynamics of the upper mantle, as they play a major role during deformation and recrystallization processes, and control partial melting of peridotites in upwelling mantle (Asimow and Langmuir, 2003; Dixon et al., 2004; Hirth and Kohlstedt, 2003; Katayama and Karato, 2008; Katz, et al., 2003). Furthermore, water has a major control on the oxidation state and on the selective enrichment in alkalies, large ion lithophile elements (LILE), and light rare earth elements (LREE) of mantle rocks (Bailey, 1982; Dixon et al., 2002; Kessel et al., 2005). Despite considerable progresses in modeling fluid behavior, our understanding of the exact nature and composition of hydrous mantle fluids is hampered by the absence of distinctive chemical signatures in many peridotites.

C-O-H fluid speciation is largely dependent on oxygen fugacity (fO2). H2O and CO2 are predicted to be the major fluid components in the shallow mantle at P ≤ 2-3 GPa, for fO2 equal to or greater than the quartz-fayalite-magnetite buffer (QFM) (Connolly, 1995; French, 1966; Huizenga, 2001, 2005; Ohmoto and Kerrick, 1977; Shi and Saxena, 1992; Zhang and Duan, 2009, 2010). Studies of gasses contained in or released from magmas, and of accessory mantle minerals (e.g., phlogopite, amphibole and apatite) suggest that fluids should contain CO2, H2O, and halogens (Marty and Tolstikhin, 1998; Marty and Zimmermann, 1999; Murck et al., 1978; Oppenheimer et al., 2011; O’Reilly and Griffin, 2000; Patino Douce et al., 2011; Smith et al., 1981; Wallace, 2003).

Fluid inclusions are the best natural samples to provide evidence for the nature of shallow-mante fluids. However, we have known for a long time that fluid inclusions in peridotites are
typically CO$_2$-rich relative to other volatiles (cf. reviews by Andersen and Neumann, 2001; Pasteris, 1987; Roedder, 1965; 1984). This discrepancy between the fluid composition observed in inclusions and that predicted by oxy-thermobarometry has bolstered models that suggest any mobile hydrous component to be partitioned to melt phases, such as silicate and carbonate melts (e.g., Luth, 2003; Murck et al., 1978; Thompson, 1992). Consequently, the apparent absence of H$_2$O has undermined the credibility of fluid inclusions as tracers of mantle processes, and has brought some authors to propose that most fluid inclusions represent late features, mainly related to deep magma degassing during ascent of peridotite xenoliths (e.g., Pasteris, 1987).

A full survey of fluid inclusions in mantle rocks does not fit the view of “pure” CO$_2$ fluids well. For example, Andersen et al. (1984) first proposed CO$_2$-brine fluids in peridotites from extensional mantle settings based on the association of carbonate and chlorine-bearing amphibole in CO$_2$ inclusions in peridotites from Bullenmeri (SE Australia). Similarly, Frezzotti et al. (2002) suggested that aggregates of talc and NaCl lining CO$_2$ inclusion cavities in olivine from peridotite of Tenerife (Canary Islands) formed as the result of post-entrapment chemical reaction between CO$_2$-brine fluids and the surrounding minerals. Recently, H$_2$O has been detected in deep diamond-bearing CO$_2$-rich fluid inclusions in garnet pyroxenites from Oahu, Hawaii (Frezzotti and Pecceirillo, 2007). In addition, brine inclusions have been described in peridotites from subduction-zone settings with increasing frequency (e.g., Hidas et al., 2010; McInnes et al., 2001; Scambelluri et al., 1997; Trial et al., 1984).

This study is aimed to check for the presence of water in fluid inclusions formed at mantle depths in several suites of metasomatized peridotite xenoliths from the Ethiopian plateau, Hawaii, and the western Mediterranean region, using Raman and Fourier transform infrared (FT-IR) microspectroscopies. We compare the present results with the results of previously published studies and critically reevaluate the composition of fluid phases at shallow-mantle depths. The present study documents that there is, or there was, a hydrous solute-rich hydrous component in
many mantle fluids trapped as inclusions. A thermodynamic model to evaluate the H$_2$O budget in shallow-mantle fluids is proposed. Although the present study focuses on mantle rocks, our approach is equally applicable to eclogites, migmatites, and granulites in the lower continental crust, where hydrous fluids are often predicted but not observed in fluid inclusions (e.g., Hollister, 1990; Touret, 1981, 2001).

1. Description of studied samples

We have investigated fluid inclusions in several suites of metasomatized spinel and garnet peridotite xenoliths. Rocks were selected from intraplate or extensional tectonic settings related recent to Plio-Quaternary volcanism. Our goal was to focus on fluid inclusions formed at mantle depths in order to study the composition of mobile mantle fluid phases. For this reason, we selected those peridotites which did not show significant melt infiltration, and where fluid inclusions did not contain glass (i.e., volatile-rich melts). Fluid inclusions were analyzed in olivine, orthopyroxene and clinopyroxene. Studied peridotites and fluid inclusions are described in the following paragraphs and presented in Table 1.

Six pargasite-bearing spinel lherzolites were selected from a suite of peridotites in Quaternary basanitic lavas from a cinder cone located in the Lake Tana region, part of the Ethiopian Plateau (Ferrando et al., 2008; Table 1). Rocks show protogranular to porphyroclastic textures and equilibrated in the lithosphere at 950–1015 °C and 1.3–2.0 GPa (Ferrando et al., 2008). Peridotites contain Cl-rich pargasite, and cryptic enrichments in Fe, Al, LILE and Pb are observed in clinopyroxene (Frezzotti et al., 2010). Coeval CO$_2$-rich fluid inclusions tiny (5–30 μm) occur in olivine and orthopyroxene porphyroclasts and subordinately in clinopyroxene, along short intragranular trails. Orthopyroxene is rich in fluid inclusions and preserves the highest density fluids (Table 1). Liquid water was detected in three CO$_2$-rich inclusions in
orthopyxene and olivine under the microscope and the heating-freezing stage. From these observations, the estimated fluid composition is $X_{\text{CO}_2} = 0.64$, $X_{\text{H}_2\text{O}} = 0.33$, $X_{\text{Na}} = 0.006$, $X_{\text{Mg}} = 0.006$, $X_{\text{Cl}} = 0.018$, and the calculated isochores indicate trapping pressures $P$, of 1.4-1.5 GPa, at 950 °C (Table 1). Modeled fluid composition is in agreement with the formation of Cl-rich metasomatic hydrous phases and with metasomatic enrichments in clinopyroxenes (Frezzotti et al., 2010). High Cl, LILE, and Pb in model metasomatic fluid phases point to a contribution of recycled altered oceanic lithosphere component in their source.

Four garnet pyroxenite samples were borrowed from the Jackson collection (Jackson and Wright, 1970) of the National Museum of Natural History (Washington D.C., USA). These are from alkali-post erosional stage Honolulu volcanics (< 1 m.y.) at Salt Lake Crater (SLC), Koolau shield, in the Island of Oahu, Hawaii (Clague and Frey, 1982; Lassiter et al., 2000; Sen, 1988). SLC garnet pyroxenites show coarse granular textures and consist of clinopyroxene (diopside-augite; > 60 % vol), olivine, orthopyroxene, garnet, and spinel. Garnet is of secondary origin, and mainly formed through exsolution from pyroxene during recrystallization processes. Although amphibole and phlogopite were previously reported (cf., Sen, 1988), traces of phlogopite were observed only in one sample. SLC garnet pyroxenites were interpreted as crystal cumulates from the recent Hawaiian volcanism in the Pacific lithosphere ($P = 1.6$-$2.2$ GPa).

Recent reports of majoritic garnet and of microdiamonds imply a much deeper origin (ca. 4.5-5 GPa; Frezzotti and Pecceclllo, 2007; Keshav and Sen, 2001, 2003; Keshav et al., 2007; Wirth and Rocholl, 2003). According to Keshav et al. (2007), garnet pyroxenites represent high-pressure cumulates related to polybaric magma fractionation in the asthenosphere. Early high-density to superdense CO$_2$ ($d = 1.16$-$1.21$ g/cm$^3$) fluid inclusions ($\leq 5$–$6$ μm) occur in clinopyroxene and subordinately in orthopyroxene, generally distributed along (010) directions. Superdense CO$_2$ is recognized by initial melting at the temperature of partial homogenization to liquid (-56.6°C; ThLs); final melting (TsL) occurs at temperatures up to - 50.8°C (Table 1; Frezzotti et al., 1992). Early inclusions contain microdiamonds and traces of H$_2$O, N$_2$ and H$_2$S.
(Frezzotti and Peccerillo, 2007), but no glass/melt. Rare carbonate inclusions, and mixed CO$_2$ + carbonate ± diamond inclusions have also been observed. These characteristics are consistent with a genetic link of fluids with ephemeral carbonate-rich melt generated in the asthenosphere within the diamond stability field (Frezzotti and Peccerillo, 2007).

Four spinel phlogopite-harzburgites and one dunite from central Italy occur in lamproitic lavas of Torre Alfina volcano (0.9-0.8 M.y.; Conticelli and Peccerillo 1990). Xenoliths consist of olivine and subordinate (3–12 vol. %) orthopyroxene porphyroclasts showing protogranular textures (Table 1). Rare anhedral clinopyroxene occurs in the interstices between deformed olivines. Brownish to black spinels are also present as isolated coarse crystals (> 1 mm) or as smaller grains. Metasomatic phlogopite is present in amounts variable from less than 1 up to 10% of the rock by mode. This has Sr-Nd ($^{87}$Sr/$^{86}$Sr ~ 0.716 - 0.717; $^{143}$Nd/$^{144}$Nd ~ 0.5121) isotopic signatures close to those of the host lamproites (Conticelli, 1998). Geothermobarometric studies indicate equilibrium pressures, $P$, of ca. 1.2-1.6 GPa, corresponding to a depth of 50 to 60 km, and temperatures, $T$, of 950–1080 °C (Pera et al., 2003; unpublished data). Rare CO$_2$-rich fluid inclusions are observed only in a few orthopyroxene porphyroclasts. Inclusions are tiny ($\leq$ 5 µm) and distributed along ⟨010⟩ directions.

Mantle melting and generation of lamproites took place during opening of Western Mediterranean basins, after the Europe-Africa continental collision. Central Italian peridotites represent samples of a “hot” lithosphere, located close to the asthenosphere-lithosphere boundary (Frezzotti et al., 2009). Metasomatism involved the presence of subducted fluids/melts of continental origin related to older subduction events of Alpine age (Peccerillo, 2005, and references therein).

Three spinel dunites and two spinel pyroxenites from Sardinia are from the spatter cone of Monte Lisiri volcano (~0.9-0.1 Ma; Lustrino et al., 2000), near the village of Ittireddu in the Logudoro region, which is part of the recent Plio-Pleistocene anorogenic alkaline mafic volcanism in northern Sardinia. Dunites show porphyroclastic textures and consist mostly of olivine porphyroclasts, with very subordinate orthopyroxene and undeformed interstitial clinopyroxene
grains. Granular pyroxenites are dominated by clinopyroxene (> 85 vol. %), with subordinate olivine and orthopyroxene. Mineral thermometry indicates relatively low temperatures (950°C). In pyroxenites, modal metasomatism is testified by the presence of phlogopite (1-2 vol. %) with high Cl contents (ca. 0.4-0.5 wt %). In dunites and pyroxenites, intragranular trails of CO$_2$-rich fluid inclusions tiny (5–20 μm) are abundant in orthopyroxene and clinopyroxene, the highest CO$_2$ densities being recorded in clinopyroxene (Table 1). In Sardinia, the origin of pyroxenites has been related to deep cumulus processes, whereas peridotites have been interpreted as upper mantle residues variably affected by metasomatic processes by melts derived from partial melting of lower crustal rocks (Lustrino et al., 2000; 2004). Peccerillo (2005), however, did not exclude that metasomatism of the lithosphere beneath northern Sardinia might have occurred by subduction-related fluids or melts in Oligo-Miocene times, based on composition of mafic rocks.

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2. Analytical Methods

Raman spectra of minerals and fluid inclusions containing C and H were acquired with a Labram microspectrometer (HORIBA Jobin Yvon) at the University of Siena. A polarized 514.5 nm water-cooled Ar-ion laser was used as the excitation source. The measured laser power was 300-500 mW at the source, and about 80% less at the sample surface. Raman spectra were collected through an OLYMPUS 100x objective (0.9 numerical aperture: excitation spot 1x1x5
µm in volume) for an acquisition time variable from 30 s to 180 s for each spectrum, and 1 to 10 accumulations. The slit width was set at 100 µm, and the corresponding spectral resolution was 1.5 cm⁻¹. Frequency wavenumbers of the Raman modes in the region 0-1800 cm⁻¹ were calibrated daily by the position of the diamond peak at 1331.7 cm⁻¹. Peak assignment of solid, gaseous, and liquid phases was done by comparison with our reference library and database of Raman spectra (http://www.dst.unisi.it/geofluids/raman/spectrum_frame.htm; Frezzotti et al., 2012).

Morphological and chemical analyses of mineral phases in open fluid inclusions were performed through scanning electron microscopy (SEM; Philips XL30) at the University of Siena. This instrument is equipped with an energy-dispersive spectrometer (EDS-Philips EDAX DX4). Selected doubly polished sections containing fluid inclusions were broken after immersion in liquid nitrogen. Broken samples were immediately mounted on stubs and carbon coated. Operating conditions were as follows: accelerating voltage 20 kV, beam current 23-25 µA, working distance 10-12 mm. Element maps with the theoretical inner pattern were obtained using the ZAF method of correction. Natural silicates and oxides have been used as standards.

To reveal water diffusion from fluid inclusions into the structure of surrounding minerals, we mapped the distribution and concentrations of structurally-bound hydrogen in nominally anhydrous minerals by synchrotron based FT-IR microspectroscopy. We selected those mantle minerals where liquid H₂O was proven in fluid inclusions: olivine and pyroxenes from Ethiopian peridotite xenoliths (Frezzotti et al., 2010), and garnet from Dora Maira whiteschists (Ferrando et al., 2009). Analyses were performed by Fourier transform infrared (FT-IR) microspectroscopy at the infrared beam-line SISSI (Source for Imaging and Spectroscopic Studies in the Infrared) operating at the synchrotron laboratory ELETTRA in Trieste. Spectra were collected on a FTIR spectrometer (Bruker IFS66/v) fitted with a Hyperion IR microscopy with a liquid-nitrogen-cooled HgCdTe (MCT) detector. Infrared microscopy was performed on an infrared microscopy system (Bruker) with a 16x magnification infrared objective. Spectra were collected at resolution
of 4 cm\(^{-1}\) and signal averaged for 128 scans on each data collection. Background spectra were recorded in air. For IR imaging studies, we used double-polished thick sections of xenoliths of known thickness. The spectral images were collected scanning areas of variable sizes (200-450 \(\mu\)m-long and 200-450 \(\mu\)m-wide), following a regular grid of square-aperture dimension of 20 \(\mu\)m equidistant by 20 \(\mu\)m in both directions (i.e., totals of 100-400 spectra), using a computer-controlled automated X-Y mapping stage. Interpretation of unpolarized spectra of \(\text{H}_2\text{O}\) followed the classical group frequency approach in which absorption bands are assigned to specific vibrational modes. OH concentrations in mineral phases were estimated from the integrated absorbance using the Beer-Lambert law (Paterson, 1982). Experimentally determined calibration constants for orthopyroxene are from Bell et al. (1995), and for olivine are from Bell et al. (2003). Since unpolarized FT-IR \(\text{H}_2\text{O}\) measurements are affected by large errors (30-50\% ; cf., Demouchy et al., 2006), and imaging revealed H variations with position within single minerals, measured water contents are reported in intervals of tens of ppm, emphasizing the relative variations with distribution within single grains. Note that, liquid \(\text{H}_2\text{O}\) and/or hydrous minerals in fluid inclusions were also suggested by FT-IR absorption bands. However, spectra are not reported in the present paper, since we consider FT-IR microspectroscopy a less reliable diagnostic technique than Raman, because of its poorer resolution, and absence of confocality.

Petrogenetic grids were calculated in the \(\text{MgO-FeO-SiO}_2-\text{H}_2\text{O-CO}_2\) (MFSHC) model system using the thermodynamic approach of Connolly (1990) and the internally consistent thermodynamic data set and equation of state for \(\text{H}_2\text{O-CO}_2\) of Holland and Powell (2011), modified considering a typical mantle \#mg \(\text{[Mg/(Mg+Fe\text{\textsuperscript{2+}})] = 0.9}\) for olivine and orthopyroxene.
3. Results

Water in CO$_2$-rich fluid inclusions is traditionally revealed by optical studies, although identification may be difficult in dense and often colored mantle minerals (cf., Roedder, 1972). Water can be detected simply by using Raman and FT-IR spectroscopic techniques (cf., Frezzotti and Peccerillo, 2007; Hidas et al., 2010; McMillan et al., 1996, and references therein). Results are given in Table 2 and discussed in the following sections. Note that the potential of Raman microspectroscopy for identifying water in mantle fluid inclusions has been known since the 80’s (e.g., Pasteris and Wanamaker, 1988). However, researchers failed to detect H$_2$O in fluid inclusions at that time, probably because of the non-confocality and lower sensitivity of old instruments.

4.1 Uncovering aqueous fluids inside inclusions: Raman spectroscopy and EDAX-EDS analyses

In almost all studied fluid inclusions H$_2$O is not visible. One exception is represented by a few relatively-large fluid inclusions (> 20 – 30 µm) in orthopyroxene of spinel lherzolites from the Ethiopian plateau, where thin (≤ 1 µm) liquid water films were recognized. In these inclusions, presence of H$_2$O was confirmed by clathrates melting during microthermometric studies at low temperatures (Table 2).

Raman microspectroscopy revealed the presence of liquid water in a minority of optically “pure” CO$_2$ fluid inclusions (10-30 µm in size), for which pyroxenes were the enclosing minerals, and a hydrous nature was recognized for the host mantle peridotites (e.g., Ethiopian plateau and Central Italy; Table 2 and Fig. 1a). For example, a Raman spectrum of liquid H$_2$O is reported in Figure 1b. The characterizing feature consists of a broad band centered approximately at 3400-3450 cm$^{-1}$ in the OH stretching region from 2900 to 3800 cm$^{-1}$. In those fluid inclusions of less than 5 µm in size, a water film rimming the CO$_2$ does not generate a discernible liquid H$_2$O Raman spectrum. However, Raman detection of H$_2$O was possible also in
these cases by spectra of isolated H₂O molecules dissolved in the CO₂ fluid (Table 2; Frezzotti and Peccerillo, 2007).

A coat of hydrous silicates and/or carbonates distributed along the rims of fluid inclusions was more commonly identified in place of molecular H₂O (Table 2; Fig. 2a-d). Talc (Tlc) was recognized by its band distribution in the OH⁻ region at 3677 cm⁻¹ (Fig. 2f). More rarely, band distribution at 3450, 3638, 3673 cm⁻¹ was observed, which corresponds to Mg-chlorite (Mg₅Al₃Si₃AlO₁₀(OH)₈; not shown). Magnesite (Mgs) was identified by its diagnostic Raman modes at 1092, 738, and 328 cm⁻¹ (Fig. 2e). Whereas the presence of carbonates in fluid inclusions was revealed by optical microscopy (Fig. 2c and d), talc and chlorite were generally overlooked. The type and amount of minerals lining CO₂-rich inclusions depend mainly on the nature of the surrounding mineral (Table 2). In olivine, hydrous silicates and carbonates are common phases (Fig. 2b and c), and in a few cases completely fill the inclusions, without any fluid left (Fig. 2d). Conversely, in orthopyroxene and clinopyroxene, while carbonates are common, hydrous silicate minerals are less frequent (Fig. 2a).

Morphological observations by SEM images inside opened fluid inclusions showed that talc is constituted by very fine flakes, forming micrometer-sized packages distributed parallel to the enclosing mineral phase along the inclusions cavity walls (Fig. 3a and b). Talc and magnesite are often glazed by a thin coating, probably precipitated during opening of fluid inclusions (Fig. 3b). SEM-EDAX spectra indicate that the coating consists of Ca, Cl, S, K, and minor Si, Na, Al and Fe (Fig. 3c). Ca and S correspond to gypsum (Raman analysis, Fig. 3d and e). Other elements suggest the presence of KCl, NaCl, and probably SiO₂ and Fe-Al oxides (Fig. 3c-e).

In clinopyroxene from hydrous peridotites (Table 1), EDS-EDAX analyses showed that CO₂-rich inclusions occur in contact with a euhedral hydrous mineral, similar in size and chemically identical to the metasomatic phase present in the rocks: pargasite in peridotites from the Ethiopian plateau (Fig. 4a and c), and phlogopite in peridotites from Sardinia (Italy) (Fig. 4b and d).
4.2 Mapping water diffusion from fluid inclusions: FT-IR spectroscopy

Mapped hydrogen gradients in olivine, orthopyroxene and garnet revealed the change from molecular water in the fluid inclusions to OH– bonds in the surrounding anhydrous minerals. Figure 5 reports the FT-IR synchrotron map of orthopyroxene and garnet hosting several fluid inclusion trails (f.i. in Fig. 5a and c). In orthopyroxene, the mapped sample area is 450x450 μm (for a total of 180 spectra), and the x-y spatial resolution is 20x20 μm (on the order of the inclusion size). The FT-IR map in Fig. 5b clearly shows an exponential increase of bonded hydrogen approaching the inclusion region. The increase of hydrogen content is evident from symmetrical differently colored haloes in orthopyroxene: calculated H₂O contents range from about 50-100 ppm far from fluid inclusions (more than 100 μm) to about 400-600 ppm, close to fluid inclusions. In garnet (mapped area 400x400 μm; x-y resolution 20x20 μm), we observed a four- to fivefold enrichment of water in areas close to fluid inclusions (Fig. 5d). Hydrogen gradients recorded by map contours represent actual water content variations in garnet with the exception of the fluid inclusion trail area where water contents above 180-200 ppm in part result from a contribution of molecular H₂O from the inclusions (red to pink areas in Fig. 5d).

In olivine (Fig. 6a; mapped area 280x280 μm; x-y resolution 20x20 μm), water enrichment is less significant than in orthopyroxene and garnet. FT-IR maps in figures 6b and c show the distribution of OH– absorption bands in two separate regions: 3000-3600 cm⁻¹ corresponding to OH– in olivine (Fig. 6b), and 3600-3800 cm⁻¹ corresponding to OH– in serpentine or talc (Fig. 6c; Khisina et al., 2001). The distribution of the strongest absorbance peak of water migration points to hydrogen diffusion from single fluid inclusions into the surrounding olivine. Presence of talc or serpentine close to fluid inclusion trails further suggest that hydration reactions occurred not only inside fluid inclusions but also in surrounding olivine (Fig. 6b).

In clinopyroxene, water enrichments close to fluid inclusion trails were not observed.
5 Discussion

5.1 There was water in fluid inclusions formed at shallow-mantle depths

The present study highlights significant dehydration of shallow-mantle fluids after trapping as inclusions. Diffusive loss of H$_2$O due to re-equilibration between the inclusion and host is demonstrated by the strong FT-IR absorbance peak of water migration in the host nominally anhydrous mantle minerals. Transport of water could have occurred under conditions of differential pressures and fluid fugacity at high $P$ and $T$ through lattice defects and microfractures. A high-concentration of dislocations around fluid inclusions was previously reported in olivine from Canary Islands peridotites, and was proposed to be the main mechanism for molecular fluid loss (Viti and Frezzotti, 2000; 2001). This diffusion-scenario is conceivable considering the extremely fast diffusion of H in olivine (Mackwell and Kohlstedt, 1990), and reinforces models proposed for selective H$_2$O loss from CO$_2$-H$_2$O inclusions in quartz (Bakker and Jansen, 1991; Romer et al., 2006; Sterner and Bodnar, 1989; Watson and Brenan, 1987).

Further, dehydration of mantle fluids is induced by reactions between residual H$_2$O fluids in the inclusions and the surrounding minerals. In magnesian olivine, the association of talc and magnesite may form at low $T$ and $P$ through the following reaction:

$$4\text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} + 5\text{CO}_2 = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 5\text{MgCO}_3$$  \hspace{1cm} (1)

However, talc and magnesite relative volumes observed in fluid inclusions (Fig. 3a) suggest that sub-equal molar amounts of these two phases were produced during the reaction, given that the molecular weight of talc is about five times that of magnesite (379 vs. 84), for similar densities (2.78 vs. 3.01 g/cm$^3$). Relative proportions of talc and magnesite can be greatly modified if H$_2$O-CO$_2$ fluids contained SiO$_2$ in solution:

$$2\text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} + \text{CO}_2 + 2\text{SiO}_2(\text{aq}) = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + \text{MgCO}_3$$  \hspace{1cm} (2)

In magnesian orthopyroxene, formation of talc and magnesite can be described by a reaction:
4MgSiO$_3$ + H$_2$O + CO$_2$ = Mg$_3$Si$_4$O$_{10}$(OH)$_2$ + MgCO$_3$  

(3)

However, while magnesite represents a common phase in fluid inclusions, talc is more rare. It is thus possible that a second reaction such as:

MgSiO$_3$ + CO$_2$ = MgCO$_3$ + SiO$_2$  

(4)

might have occurred between H$_2$O-CO$_2$ fluids of variable $X_{H2O}$ and surrounding orthopyroxene. In contrast, fluid inclusions in clinopyroxene do not seem to contain or have contained H$_2$O. Talc and magnesite are rare, and FT-IR absorption maps do not show significant water enrichments. This result is surprising, given that the capacity of clinopyroxene to store H$_2$O greatly exceeds that of olivine at upper mantle pressures (Aubaud et al, 2004). Although we may have overlooked some processes, as the studied clinopyroxene is from hydrous peridotites where metasomatic amphibole or phlogopite are present, our preferred explanation for the analytical data is that reaction of the hydrous fluid occurred along microfractures at the infiltration stage, prior to inclusion formation. Hydration of clinopyroxene during microfracture healing is suggested by formation of tiny pargasite (or phlogopite) grains, occurring with CO$_2$ fluid inclusions along the same microfracture (Fig. 4). In olivine and orthopyroxene, similar hydration reactions are inhibited, since they occur at lower temperatures below most mantle geotherms (see also section 5.2), and hydrous mantle fluids are trapped inside inclusions. Interestingly, Lamb et al. (1987) proposed a similar evolution to explain selective CO$_2$ enrichments observed in fluid inclusions of some high-grade metamorphic rocks.

5.2 Amounts of water in shallow-mantle fluids

A critical question to petrological and geophysical studies is how much water was originally present in shallow-mantle fluids. This issue can be investigated by modeling the reactions between H$_2$O-CO$_2$ fluid inclusions and surrounding magnesian orthopyroxene (Mg/Mg+Fe=0.9)
in peridotites. For magnesian olivine, similar reactions cannot be modeled since they require SiO$_2$ in the fluid (cf., reaction 2 in 5.1). Figure 7 shows $T$-X$_{H_2O}$ phase diagrams for the MFSHC model system at different pressures. The model reactions can be used to simulate the chemical re-equilibrations between aqueous-carbonic fluids with different X$_{H_2O}$ in inclusions and surrounding orthopyroxene. These diagrams show that the minimum X$_{H_2O}$ necessary to induce hydration reactions between fluid inclusions and surrounding minerals increases with increasing fluid pressure. If we consider the formation of talc inside a fluid inclusion in orthopyroxene, a $T$ of 1 GPa, the minimum X$_{H_2O}$ is 0.25 (see invariant point 1 in Fig. 7b), while at 0.5 GPa, it decreases to X$_{H_2O}$ = 0.1 (invariant point 1 in Fig. 7c). The maximum X$_{H_2O}$ should not exceed 0.5 regardless of pressure, since ensuing reactions would consume equal amounts of H$_2$O and CO$_2$, whereas observed fluid inclusions have CO$_2$-rich compositions. From figure 7, it is also evident that reactions between H$_2$O-CO$_2$ fluid inclusions and the surrounding minerals cannot be a mantle process, as talc and/or magnesite only forms as temperatures decrease below about 700-600°C for variable pressures. We propose that eruption provides the conditions to induce reactions. In explosive eruptions, temperatures of xenoliths fall below 600°C over 5-10 sec. of ballistic transport through the air (Shaw, 2009). Even in slower-cooling lavas, xenoliths take only a few hours to reach the same temperatures.

A strong dependency on pressure for hydrous fluid inclusion evolution is illustrated in Figure 8. Consider a dense CO$_2$-H$_2$O fluid inclusion with X$_{H_2O}$=0.3 in orthopyroxene formed at 1.5 GPa and 1000°C in a mantle peridotite. When this inclusion ascends rapidly and adiabatically in a xenolith within the host magma, it will effectively become overpressurized (path a in Fig. 8). If decrepitation does not occur, it arrives at the surface, and subsequent syn-, and post-eruptive decrease of temperature will cool the fluid in the inclusion along an isochore (path b in Fig. 8). At temperatures below approximately 700°C, CO$_2$-H$_2$O fluid reaction with surrounding minerals promotes the formation of magnesite in inclusions, but not hydrous phases (i.e., reaction 4 in 5.1). As far as a fluid inclusion remains overpressurized during adiabatic ascent and cooling,
hydrous phases cannot form. When the same fluid inclusion decrpetitates during ascent, so that fluid density resets to a lower value corresponding, for example, to $P < 1 \text{GPa}$ (below point 1 in Fig. 8), syneruptive cooling along isochore (path c in Fig. 8) would make the CO$_2$-H$_2$O fluids in the inclusion to react to form talc + magnesite (reaction 3 in 5.1).

In summary, thermodynamic modeling suggests that up to 50 mole % water should have been present in fluid inclusions formed at mantle depths in order to drive the observed reactions in orthopyroxene. Petrogenetic grids also show that syneruptive cooling in host peridotite xenoliths promotes fluid reactions with surrounding minerals. Lower overpressures in the fluid inclusion require a lower minimum water amount in the fluid in order for hydration reactions to take place. It appears reasonable to conclude that hydration reactions associated with diffusive water loss reset fluid inclusions to the minimum concentration of H$_2$O and produce a dehydration trend which may result in the “pure CO$_2$” inclusions often described in mantle minerals. It is noteworthy to recall that any geobarometric data derived from similar CO$_2$-rich inclusions could result in underestimates, since CO$_2$-rich fluids would have residual composition and density considerably lower than that of the original mantle fluids at the time of entrapment.

5.3 Reevaluation of shallow-mantle fluid composition

In the absence of pristine inclusions in mantle minerals, an accurate characterization of the chemistry of the aqueous fluid component is complicated. Even so, the identity of minerals precipitating inside fluid inclusions through reactions with surrounding minerals gives information on the nature of species in solution. Ubiquitous talc forming through fluid reaction with surrounding host phases indicates Si as a major solute component (cf., reactions 2 and 3 in 5.1). Additionally, relevant amounts of Cl, S, Ca, K, and Na are revealed by chlorides and gypsum precipitated in inclusions on cooling. Interestingly, K seems to be present in relatively higher amounts than Na. Sulfur has been identified either as hydrogen sulfide gas (H$_2$S), elemental sulfur ($S_8$), or as sulfate ions (hydrated form of SO$_3$) (Table 1) depending on the
oxidation state of the fluid, and indeed sulfur appears to bear a major control over the oxidation state. The sulfate ions detected in some fluid inclusions are a real feature, since, eventual postentrapment fluid inclusion redox-reactions would tend to reduce sulfur (Grishina et al., 1992).

The model composition of saline multicomponent mantle fluids that emerges from the present study is in agreement with formation of Cl-rich hydrous metasomatic phases and with extreme LILE enrichments in the studied peridotites (cf., section 2). In addition, the applicability of new chemical data to natural mantle fluids is supported by studies on major element solubility at high $P$ and $T$. Experimental data up to 3 GPa and 1300°C indicate alkalis as the most soluble species in aqueous fluids, followed by Cl, Si, and Ca, while Mg and Fe are relatively less soluble (Brenan et al., 1995; Dvir et al., 2011; Eggler, 1987; Kawamoto et al., 2004; Manning, 2004; Nakamura and Kushiro, 1974; Newton and Manning, 2002; Stalder et al., 2001). For example, Nakamura and Kushiro (1974) estimated that 20 wt. % silica is dissolved in H$_2$O fluids coexisting with mantle enstatite at 1.5 GPa and 1280°C. The presence of CO$_2$ in the fluid strongly depresses the solubility of silica, while the presence of chlorine has the opposite effect (cf., Newton and Manning, 2010).

Previous direct measurements indicated that 10-14 wt% solutes (in NaCl equivalent) are present in hydrous fluid inclusions from the Ethiopian plateau (see section 2). Measured solute concentrations are in agreement with 2.5 wt% Cl (or 3.5-9 wt. % in NaCl equivalent) predicted for mantle fluids (Burgess and Turner, 1995), and with 6-10 wt % solutes measured in H$_2$O-rich subduction fluids (1-2 GPa; Manning, 2004). The total fluid solute content cannot have been extreme in order to trap homogeneous fluids in inclusions (Figs. 1 and 2). High-salinity aqueous fluids, having a large immiscibility solvus in the CO$_2$-H$_2$O-NaCl system, would have been immiscible with CO$_2$ at the considered mantle $P$-$T$ conditions (Touret, 1992; 2009). Phase separation (into L+V) would have formed distinct CO$_2$-rich and saline-aqueous fluid inclusions in mantle minerals, which have not been observed. Based on these observations, the concentrated
brines (NaCl ≥ 50 wt %; Scambelluri et al., 1997) described in fluid inclusions of some peridotites from subduction settings are likely to reflect the evolution of multicomponent fluids towards increasing solute/H$_2$O ratios either by decompression-induced phase separation in the CO$_2$-H$_2$O-salt fluid system, or by postentrapment inclusion “dehydration” trends.

**5.4 Origin of water and chlorine in shallow-mantle fluids**

Cl-bearing hydrous fluids may be common in subduction zones, generated by the breakdown of hydrous minerals (e.g., serpentine; Manning, 2004; Poli and Schmidt, 2002; Scambelluri et al., 2001; Sharp and Barnes, 2004). Thus, peridotites from mantle wedges are the best candidates to find hydrous fluid inclusions. In this respect, fluid inclusions in peridotites from Central Italy and Sardinia may testify to metasomatic fluids released during old subduction events. As noted by Peccerillo (2005), in Italy and the southern Tyrrhenian sea, Plio-Quaternary magma generation does not necessarily need to be coeval with subduction and mantle metasomatism; it may postdate these processes, and could be triggered by changes in thermal regimes in the upper mantle.

Our data raise the question of the origin of aqueo-carbonic fluids carrying significant amounts of Cl in the lithosphere within the context of intraplate and extensional mantle settings (e.g., Ethiopia, and Hawaii) (Le Roux et al., 2006; Michael and Schilling, 1989; Seaman et al., 2004; Stolper et al., 2004). In the east African lithosphere, evidence for mantle metasomatism driven by Cl-bearing hydrous fluids is consistently reported from several xenolith localities and supposed to have occurred during the early stages of mantle upwelling. The Cl-pargasite bearing lithosphere under the Ethiopian plateau is considered to have been modally metasomatized by CO$_2$-brine fluids, probably derived by degassing of deep carbonate rich melts during early stages of upwelling of the Afar mantle zone (Frezzotti et al., 2010). Additionally, Cl-rich pargasite in spinel lherzolites of Zabargad Island is interpreted to have formed just before the early rifting phase of the Red Sea (Agrinier et al., 1993). In a similar way, the growth of amphibole ± Cl-
apatite in spinel peridotites from Yemen has been proposed to have been induced by the influx of carbonatitic melts and hydrous fluids from the Afar plume during the Oligocene (Baker et al., 1998). At Hawaii, Iceland, and Azores, Cl-enrichment in the lithosphere is indicated by the high Cl/F ratios of melt inclusions in OIB (e.g., Dixon et al., 2008; Le Roux et al., 2006; Michael and Schilling, 1989; Seaman et al., 2004; Stolper et al., 2004).

There should be other water and Cl-sources besides active subduction. Evidence for hydrous mantle fluids away from subduction zones has been obtained in cratonic areas by fluid inclusions in fibrous diamonds, where fluids consist of three main components: a carbonate melt, a silicate melt, and a hydro-saline fluid (e.g., Izraeli et al., 2001; Klein-BenDavid et al., 2004; 2007; Kopylova et al., 2010; Navon et al., 1988). The hydrous fluid component is enriched in SiO$_2$, Al$_2$O$_3$, halides, and alkalis (mainly K), similar to shallower hydrous fluids reported by this study. The total solute content is, however, considerably higher in diamond fluids (e.g., Cl up to ca. 35 wt. %), possibly reflecting the increase of elements solubility at greater $P$ and $T$ ($P \geq 4-5$ GPa; e.g., supercritical fluid phases; Bureau and Keppler, 1999; Kawamoto et al., 2004; Kessel et al., 2005; Manning, 2004). In diamonds, continuous compositional variations of fluid inclusions are observed, suggesting that all components might be genetically related, most likely evolved from a “primitive” carbonate-rich melt (cf., Klein-BenDavid et al., 2004, and references therein).

Recent experimental evidence shows that immiscibility processes in this silicate–carbonate–H$_2$O system facilitate the chlorine enrichment of the carbonate melt or of the aqueous fluid, not only at high pressures in the diamond stability field, but also at lithospheric pressures (Litasov and Ohtani, 2009; Litasov et al., 2011; Safonov, 2011).

It is conceivable to suppose that Cl-bearing hydrous shallow mantle fluids might have been formed through hydro-saline carbonate melts. As mentioned above, the model composition of hydrous shallow mantle fluids in spinel peridotites is similar to that of the aqueous fluid component trapped deeper, in diamonds. Further comparisons are difficult because of the limited data. Fluxes of CO$_2$-H$_2$O and Cl in the lithosphere could have been generated by degassing of
upwelling carbonate-rich melts at pressures below the carbonate-stability field (2–2.5 GPa; Dobson et al., 1996; Hammouda and Laporte, 2000). Since fluid data from mantle rocks in intraplate and extensional tectonic settings are limited, it is not known whether carbonate-melt degassing may be the main source of lithospheric hydrous fluids, or some other mechanisms, such as silicate melt – fluid immiscibility, have to be invoked. In any case, the deep association of CO₂, H₂O, carbonates, and diamonds preserved in fluid inclusions of Hawaiian garnet pyroxenites (Frezzotti an Peccerillo, 2007) was interpreted to have caught this process in the act.

6. Conclusions

The methodology presented in this paper shows that water is an elusive component in fluid inclusions in many hydrous and anhydrous upper mantle peridotites (i.e., Hawaii, Ethiopia, Canary Islands, and the western Mediterranean region). In shallow-mantle rocks, “pure CO₂” inclusions observed optically should be considered to contain less than 20 mole % of H₂O, in absence of spectroscopic analysis. Raman identification of H₂O, as OH⁻, bound in hydrous silicates lining fluid inclusions suggests that hydrous fluid/host mineral chemical reactions represent a common postentrapment process, leading to fluid inclusion dehydration. FT-IR analysis of the distribution of water enrichment in mantle minerals suggests further dehydration through decrepitation, stretching, and H₂O diffusion.

Although shallow mantle fluids are generally dominated by CO₂, constraints from thermodynamic modeling in the MFSHC system suggest that up to 50 mole % H₂O could be present. Water activity (aH₂O) is expected to be low (probably < 0.4), in agreement with the anhydrous nature of many peridotite xenoliths. However, the existence of a hydrous fluid component will influence the physical and chemical evolution of the shallow mantle. Presence of H₂O and solutes makes migration of fluids more effective (Mibe et al., 1998, 1999; 2002; Watson and Brenan. 1987). Moreover, the solute content in such hydrous fluids will affect
transport and partitioning of elements inducing metasomatism in mantle rocks (Ayers, 1998; Keppler, 1996; Kessel et al., 2005; Konrad-Schmolke et al., 2011).

In extending present results to a broad statement about the composition of shallow-mantle fluid inclusions, we propose that multicomponent fluids are widespread in the shallow mantle, not only in subduction-zone settings, but also in extensional or intraplate settings. However, a stronger validation requires further spectroscopic (re)investigation of fluid inclusions in mantle peridotites.

Acknowledgments

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00175-6.


Captions to Figures

Fig. 1 - Raman detection of optically hidden liquid water in fluid inclusions. a) Trail of fluid inclusions in orthopyroxene. White asterisks indicate those fluid inclusions where liquid H$_2$O was detected by Raman spectroscopy. b) Raman spectrum of liquid H$_2$O rimming CO$_2$ in a fluid inclusion in Fig. 2a.

Fig. 2 - Different extents of fluid inclusion-host reactions as detected by Raman microspectroscopy. Inclusions show textural evidence for an increasing reaction degree with the enclosing mineral going from microphotographs a-b, to c and d. a) Decrepitated high-density (monophase) CO$_2$ fluid inclusion containing magnesite (Mgs) in orthopyroxene. b) Magnesite (Mgs) and talc (Tlc) in apparently preserved high density (monophase) CO$_2$ fluid inclusions distributed along a trail in olivine. c) Decrepitated and reacted fluid inclusion in olivine. Inclusion contains two phase (liquid + vapor) CO$_2$, Mgs, and Tlc. d) Decrepitated and reacted fluid inclusion in olivine. The inclusion is filled by aggregates of Tlc and Mgs, with no visible fluid left. e) Raman modes of magnesite inside fluid inclusions. Unlabelled peaks refer to enclosing olivine. f) OH$^-$ Raman modes of talc recorded inside fluid inclusions.

Fig. 3 - EDS-EDAX and Raman analyses in open fluid inclusions. a) Electron microphotograph of an open inclusion in olivine. Talc (Tlc) and magnesite (Mgs) coat the inclusion walls. b) Electron microphotograph of an open fluid inclusion in orthopyroxene. Tlc is distributed along the inclusion walls. A thin microcrystalline coating of gypsum, KCl, NaCl, SiO$_2$, and Fe-Al oxides is observed on talc crystals (inset). c) Qualitative EDS-EDAX chemical analysis of the coating shown in Fig. 3b (inset image). d) Main Raman modes of gypsum inside the fluid inclusion in Fig. 3b. Unlabelled peaks refer to enclosing orthopyroxene. e) OH$^-$ Raman modes of...
gypsum. Raman spectra in Fig. 3d and e were collected in the same area of EDS-EDAX analysis (inset image in 3b).

Fig. 4 - Association of fluid, and hydrous-silicate inclusions in clinopyroxene (Cpx) from hydrous peridotites. a) Photomicrograph showing trailbound fluid inclusions (f.i.) and pargasite (Prg) in Cpx in peridotites from Ethiopia. b) Photomicrograph showing trailbound fluid inclusions (f.i.) and phlogopite (Phl) in Cpx in peridotites from Sardinia. c) Back scattered electron image showing f.i. (black) and Prg (dark gray) distribution in Cpx. Spinel inclusions are also visible (white). Back scattered electron image image of f.i. (black) and Phl distribution in Cpx. Note that Phl and Prg inclusions have the same chemical composition as metasomatic phases in rocks.

Fig. 5 - Synchrotron FT-IR imaging of water distribution in orthopyroxene and garnet surrounding fluid inclusions. (a) Microphotograph showing fluid inclusion (f.i.) distribution in the investigated orthopyroxene area, plane polarized light. (b) Absorbance map in the 3000–3600 cm⁻¹ region and calculated water contents in Opx (ppm). (c) Microphotograph of garnet containing fluid inclusions (f.i.), crossed polars. (e) Absorbance map in the 3000–3800 cm⁻¹ region and relative calculated water contents in Grt (ppm). In FT-IR maps, the color scale is proportional to OH⁻ enrichment (increasing from blue to pink). Measured water contents are drawn with a precision of 20’s of ppm. Ol = olivine; Spl = spinel.

Fig. 6 - Synchrotron FT-IR imaging of water distribution in olivine. Microphotograph of investigated area in olivine containing several fluid inclusions. b) Absorbance map in the 3000–3600 cm⁻¹ region and calculated water contents in olivine (ppm). The color scale is proportional to OH⁻ enrichment (increasing from blue to pink). Measured water contents are drawn with a precision of 10’s of ppm. c) Qualitative distribution map of OH absorbance for talc and
serpentine in the 3600–3800 cm\(^{-1}\) region, which allows to qualify hydrated phases in olivine.

a.u.: arbitrary units.

Fig. 7 – \(T-X_{H_2O}\) petrogenetic grids at 1.5 GPa, 1.0 GPa, 0.5 GPa, and 0.1 GPa in the MgO-FeO-SiO\(_2\)-H\(_2\)O-CO\(_2\) system, calculated with En and Fo compositions at \#mg = 0.9, calculated with the thermodynamic approach of Connolly (1990). White dots are the invariant points. Black solid curves highlight possible reactions between H\(_2\)O-CO\(_2\) fluids trapped in inclusions and the surrounding magnesian orthopyroxene. All reaction equations are written such that the high-X\(_{CO2}\) assemblage is on the right side. The occurrence of talc as product of reactions depends on fluid pressure and on \(X_{H2O}\) (invariant point 1), see 5.2.

Fig. 8 - \(P-T\) petrogenetic grid at \(X_{H2O} = 0.3\) in the MgO-FeO-SiO\(_2\)-H\(_2\)O-CO\(_2\) system, calculated with En and Fo compositions at \#mg = 0.9. White dots are the invariant points. Black thick solid curves highlight possible reactions between H\(_2\)O-CO\(_2\) fluids trapped in inclusions and the surrounding orthopyroxene. All reaction equations are written such that the low-\(X_{H2O}\) assemblage is on the right side. The oval and the star indicate the \(P-T\) conditions of fluid inclusion trapping and fluid inclusion decrepitation, respectively. The thick black arrow (a) represents the \(P-T\) path of a mantle xenolith within the host lava. The dashed grey lines represent isochores of preserved (b), and decrepitated (c) fluid inclusions. The two thin black arrows represent the \(P-T\) paths of preserved (high density, isochore b), and decrepitated (low density, isochore c) fluid inclusions. As evident from the grid, syn-, and post-eruptive reactions between fluid inclusions and surrounding orthopyroxene can produce hydrous minerals (talc) only in low-density fluid inclusions (c).
• Raman and FTIR in fluid inclusions can verify the hydrous nature of mantle fluids.
• Shallow mantle inclusions either contain H₂O or represent “dehydrated” fluids.
• Hydrous fluid inclusions carry significant amounts of Si, Cl, S, K, Ca, and Na.
• Solute-rich hydrous fluids may be widespread in the shallow mantle.
Figure 1
Click here to download Figure: Fig. 1.eps
Figure 2
Click here to download Figure: Fig. 2.eps
Figure 3

Click here to download Figure: Fig. 3.eps

(a) SEM image with labeled elements: Ca, K, Cl, Si, Al, Fe, Na, S, Mg, and Tlc.

(b) Magnified view with labeled elements: Ca, Mg, S, and Tlc.

(c) Element distribution chart showing peaks for Na, Al, Si, S, Cl, K, and Fe.

(d) Gypsum spectrum with peaks at 414, 494, and 1008 cm⁻¹.

(e) Gypsum - OH spectrum with peaks at 3405, 3490 cm⁻¹.
Figure 4
Click here to download Figure: Fig. 4.eps
OH in Talc and Serpentine

H₂O content in olivine

Figure 6
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$X_{H_2O} = 0.3$
### Table 1 - Sample description

<table>
<thead>
<tr>
<th>Locality</th>
<th>Host rock</th>
<th>Rock type</th>
<th>Texture</th>
<th>Mineralogy</th>
<th>P-T conditions</th>
<th>CO$_2$-rich fluid inclusions</th>
<th>P from isochores</th>
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Ol = Olivine; Opx = Orthopyroxene; Cpx = Clinopyroxene; Spl = Spinel; Grt = Garnet; Prg = Pargasite; Phi = Phlogopite; Tm = temperature of melting; ThL = temperature of homogenization to liquid; ThsL = temperature of homogenization to liquid in presence of solid CO$_2$; TsL = temperature of solid CO$_2$ final melting; ThsL = temperature of solid CO$_2$ final melting; superdense CO$_2$ inclusions; Hhl = hydrohalite; Clat = clathrate; Ol1, Opx1 = olivine and orthopyroxene porphyroclasts; * Pressures derived from Raman CO$_2$ density data (cf., Frezzotti et al., 2012).
Table 2 - Detection of water and solutes in fluid inclusions in mantle mineral using different analytical techniques

<table>
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<tr>
<th>Locality</th>
<th>Rock type</th>
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<th>Host Mineral</th>
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<td>No</td>
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Ol = Olivine; Opx = Orthopyroxene; Cpx = Clinopyroxene; Sp = Spinel; Grt = Garnet; Prg = Pargasite; Phl = Phlogopite; Lherz. = Lherzolite; Harz. = Harzburgite; Dun. = Dunite; Pyrox. = Pyroxenite; f.i. = Fluid inclusions; Microsc. = Microscopy; Microther. = Microthermometry; * = not analyzed. * data from Frezzotti et al., 2002a.