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Water content and nature of solutes

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in shallow-mantle fluids from fluid inclusions

4

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13

14 **Abstract**

15

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

32

33 **Keywords:** Mantle petrology, Upper mantle fluid, fluid inclusions, Raman spectroscopy, FT-IR
34 spectroscopy

35 **Introduction**

36
37

38 The volatile (e.g., C, O, H and halogens) inventory in the Earth's upper mantle includes
39 accessory phases, nominally anhydrous minerals (NAMS), along with mobile fluid phases and
40 volatile-rich melts (e.g., Bell et al., 2003; Bolfan-Casanova et al., 2000; Dasgupta and
41 Hirschmann, 2006; Green and Falloon, 1998; Thompson, 1992; Wyllie and Ryabchikov, 2000).
42 Hydrous fluids are critical to understand the structure and dynamics of the upper mantle, as they
43 play a major role during deformation and recrystallization processes, and control partial melting
44 of peridotites in upwelling mantle (Asimow and Langmuir, 2003; Dixon et al., 2004; Hirth and
45 Kohlstedt, 2003; Katayama and Karato, 2008; Katz, et al., 2003). Furthermore, water has a major
46 control on the oxidation state and on the selective enrichment in alkalis, large ion lithophile
47 elements (LILE), and light rare earth elements (LREE) of mantle rocks (Bailey, 1982; Dixon et
48 al., 2002; Kessel et al., 2005). Despite considerable progresses in modeling fluid behavior, our
49 understanding of the exact nature and composition of hydrous mantle fluids is hampered by the
50 absence of distinctive chemical signatures in many peridotites.

51 C-O-H fluid speciation is largely dependent on oxygen fugacity (fO_2). H_2O and CO_2 are
52 predicted to be the major fluid components in the shallow mantle at $P \leq 2-3$ GPa, for fO_2 equal to
53 or greater than the quartz-fayalite-magnetite buffer (QFM) (Connolly, 1995; French, 1966;
54 Huizenga, 2001, 2005; Ohmoto and Kerrick, 1977; Shi and Saxena, 1992; Zhang and Duan,
55 2009, 2010). Studies of gasses contained in or released from magmas, and of accessory mantle
56 minerals (e.g., phlogopite, amphibole and apatite) suggest that fluids should contain CO_2 , H_2O ,
57 and halogens (Marty and Tolstikhin, 1998; Marty and Zimmermann, 1999; Murck et al., 1978;
58 Oppenheimer et al., 2011; O'Reilly and Griffin, 2000; Patino Douce et al., 2011; Smith et al.,
59 1981; Wallace, 2003).

60 Fluid inclusions are the best natural samples to provide evidence for the nature of shallow-
61 mantle fluids. However, we have known for a long time that fluid inclusions in peridotites are

62 typically CO₂-rich relative to other volatiles (cf. reviews by Andersen and Neumann, 2001;
63 Pasteris, 1987; Roedder, 1965; 1984). This discrepancy between the fluid composition observed
64 in inclusions and that predicted by oxy-thermobarometry has bolstered models that suggest any
65 mobile hydrous component to be partitioned to melt phases, such as silicate and carbonate melts
66 (e.g., Luth, 2003; Murck et al., 1978; Thompson, 1992). Consequently, the apparent absence of
67 H₂O has undermined the credibility of fluid inclusions as tracers of mantle processes, and has
68 brought some authors to propose that most fluid inclusions represent late features, mainly related
69 to deep magma degassing during ascent of peridotite xenoliths (e.g., Pasteris, 1987).

70 A full survey of fluid inclusions in mantle rocks does not fit the view of “pure” CO₂ fluids
71 well. For example, Andersen et al. (1984) first proposed CO₂-brine fluids in peridotites from
72 extensional mantle settings based on the association of carbonate and chlorine-bearing
73 amphibole in CO₂ inclusions in peridotites from Bullenmeri (SE Australia). Similarly, Frezzotti
74 et al. (2002a, and b) suggested that aggregates of talc and NaCl lining CO₂ inclusion cavities in
75 olivine from peridotite of Tenerife (Canary Islands) formed as the result of post-entrapment
76 chemical reaction between CO₂-brine fluids and the surrounding minerals. Recently, H₂O has
77 been detected in deep diamond-bearing CO₂-rich fluid inclusions in garnet pyroxenites from
78 Oahu, Hawaii (Frezzotti and Peccerillo, 2007). In addition, brine inclusions have been described
79 in peridotites from subduction-zone settings with increasing frequency (e.g., Hidas et al., 2010;
80 McInnes et al., 2001; Scambelluri et al., 1997; Trial et al., 1984).

81 This study is aimed to check for the presence of water in fluid inclusions formed at mantle
82 depths in several suites of metasomatized peridotite xenoliths from the Ethiopian plateau,
83 Hawaii, and the western Mediterranean region, using Raman and Fourier transform infrared (FT-
84 IR) microspectroscopies. We compare the present results with the results of previously published
85 studies and critically reevaluate the composition of fluid phases at shallow-mantle depths. The
86 present study documents that there is, or there was, a hydrous solute-rich hydrous component in

87 many mantle fluids trapped as inclusions. A thermodynamic model to evaluate the H₂O budget in
88 shallow-mantle fluids is proposed. Although the present study focuses on mantle rocks, our
89 approach is equally applicable to eclogites, migmatites, and granulites in the lower continental
90 crust, where hydrous fluids are often predicted but not observed in fluid inclusions (e.g.,
91 Hollister, 1990; Touret, 1981, 2001).

92

93 1. Description of studied samples

94

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

103 Six pargasite-bearing spinel lherzolites were selected from a suite of peridotites in Quaternary
104 basaltic lavas from a cinder cone located in the Lake Tana region, part of the Ethiopian Plateau
105 (Ferrando et al., 2008; Table 1). Rocks show protogranular to porphyroclastic textures and
106 equilibrated in the lithosphere at 950–1015 °C and 1.3–2.0 GPa (Ferrando et al., 2008).
107 Peridotites contain Cl-rich pargasite, and cryptic enrichments in Fe, Al, LILE and Pb are
108 observed in clinopyroxene (Frezzotti et al., 2010). Coeval CO₂-rich fluid inclusions tiny (5–30
109 μm) occur in olivine and orthopyroxene porphyroclasts and subordinately in clinopyroxene,
110 along short intragranular trails. Orthopyroxene is rich in fluid inclusions and preserves the
111 highest density fluids (Table 1). Liquid water was detected in three CO₂-rich inclusions in

112 orthopyroxene and olivine under the microscope and the heating-freezing stage. From these
113 observations, the estimated fluid composition is $X_{\text{CO}_2} = 0.64$, $X_{\text{H}_2\text{O}} = 0.33$, $X_{\text{Na}} = 0.006$, $X_{\text{Mg}} =$
114 0.006 , $X_{\text{Cl}} = 0.018$, and the calculated isochores indicate trapping pressures, P , of 1.4-1.5 GPa,
115 at 950 °C (Table 1). Modeled fluid composition is in agreement with the formation of Cl-rich
116 metasomatic hydrous phases and with metasomatic enrichments in clinopyroxenes (Frezzotti et
117 al., 2010). High Cl, LILE, and Pb in model metasomatic fluid phases point to a contribution of
118 recycled altered oceanic lithosphere component in their source.

119 Four garnet pyroxenite samples were borrowed from the Jackson collection (Jackson and
120 Wright, 1970) of the National Museum of Natural History (Washington D.C., USA). These are
121 from alkali-post erosional stage Honolulu volcanics (< 1 m.y.) at Salt Lake Crater (SLC), Koolau
122 shield, in the Island of Oahu, Hawaii (Clague and Frey, 1982; Lassiter et al., 2000; Sen, 1988).
123 SLC garnet pyroxenites show coarse granular textures and consist of clinopyroxene (diopside-
124 augite; > 60 % vol), olivine, orthopyroxene, garnet, and spinel. Garnet is of secondary origin,
125 and mainly formed through exsolution from pyroxene during recrystallization processes.
126 Although amphibole and phlogopite were previously reported (cf., Sen, 1988), traces of
127 phlogopite were observed only in one sample. SLC garnet pyroxenites were interpreted as crystal
128 cumulates from the recent Hawaiian volcanism in the Pacific lithosphere ($P = 1.6\text{-}2.2$ GPa).
129 Recent reports of majoritic garnet and of microdiamonds imply a much deeper origin (ca. 4.5-5
130 GPa; Frezzotti and Peccerillo, 2007; Keshav and Sen, 2001, 2003; Keshav et al., 2007; Wirth
131 and Rocholl, 2003). According to Keshav et al. (2007), garnet pyroxenites represent high-
132 pressure cumulates related to polybaric magma fractionation in the asthenosphere. Early high-
133 density to superdense CO_2 ($d = 1.16\text{-}1.21$ g/cm³) fluid inclusions ($\leq 5\text{-}6$ μm^3) occur in
134 clinopyroxene and subordinately in orthopyroxene, generally distributed along (010) directions.
135 Superdense CO_2 is recognized by initial melting at the temperature of partial homogenization to
136 liquid (-56.6°C; ThLs); final melting (TsL) occurs at temperatures up to - 50.8°C (Table 1;
137 Frezzotti et al., 1992). Early inclusions contain microdiamonds and traces of H_2O , N_2 and H_2S

138 (Frezzotti and Peccerillo, 2007), but no glass/melt. Rare carbonate inclusions, and mixed CO₂ +
139 carbonate ± diamond inclusions have also been observed. These characteristics are consistent
140 with a genetic link of fluids with ephemeral carbonate-rich melt generated in the asthenosphere
141 within the diamond stability field (Frezzotti and Peccerillo, 2007).

142 Four spinel phlogopite-harzburgites and one dunite from central Italy occur in lamproitic lavas of
143 Torre Alfina volcano (0.9-0.8 M.y.; Conticelli and Peccerillo 1990). Xenoliths consist of olivine
144 and subordinate (3–12 vol. %) orthopyroxene porphyroclasts showing protogranular textures (Table
145 1). Rare anhedral clinopyroxene occurs in the interstices between deformed olivines. Brownish to
146 black spinels are also present as isolated coarse crystals (> 1 mm) or as smaller grains. Metasomatic
147 phlogopite is present in amounts variable from less than 1 up to 10% of the rock by mode. This has
148 Sr-Nd (⁸⁷Sr/⁸⁶Sr ~ 0.716 - 0.717; ¹⁴³Nd/¹⁴⁴Nd ~ 0.5121) isotopic signatures close to those of the host
149 lamproites (Conticelli, 1998). Geothermobarometric studies indicate equilibrium pressures, *P*, of ca.
150 1.2-1.6 GPa, corresponding to a depth of 50 to 60 km, and temperatures, *T*, of 950–1080 °C (Pera et
151 al., 2003; unpublished data). Rare CO₂-rich fluid inclusions are observed only in a few
152 orthopyroxene porphyroclasts. Inclusions are tiny (≤ 5 μm) and distributed along (010) directions.

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

159 Three spinel dunites and two spinel pyroxenites from Sardinia are from the spatter cone of
160 Monte Lisiri volcano (~0.9-0.1 Ma; Lustrino et al., 2000), near the village of Ittireddu in the
161 Logudoro region, which is part of the recent Plio-Pleistocene anorogenic alkaline mafic volcanism
162 in northern Sardinia. Dunites show porphyroclastic textures and consist mostly of olivine
163 porphyroclasts, with very subordinate orthopyroxene and undeformed interstitial clinopyroxene

164 grains. Granular pyroxenites are dominated by clinopyroxene (> 85 vol. %), with subordinate
165 olivine and orthopyroxene. Mineral thermometry indicates relatively low temperatures (950°C). In
166 pyroxenites, modal metasomatism is testified by the presence of phlogopite (1-2 vol. %) with high
167 Cl contents (ca. 0.4-0.5 wt %). In dunites and pyroxenites, intragranular trails of CO₂-rich fluid
168 inclusions tiny (5–20 μm) are abundant in orthopyroxene and clinopyroxene, the highest CO₂
169 densities being recorded in clinopyroxene (Table 1). In Sardinia, the origin of pyroxenites has been
170 related to deep cumulus processes, whereas peridotites have been interpreted as upper mantle
171 residues variably affected by metasomatic processes by melts derived from partial melting of lower
172 crustal rocks (Lustrino et al., 2000; 2004). Peccerillo (2005), however, did not exclude that
173 metasomatism of the lithosphere beneath northern Sardinia might have occurred by subduction-
174 related fluids or melts in Oligo-Miocene times, based on composition of mafic rocks.

175 Among selected samples, pyrope garnet is present only in Hawaiian pyroxenites, and it does
176 not contain mantle fluid inclusions. In order to study the post-entrapment evolution of fluid
177 inclusions in garnet, we additionally included one sample of whiteschist from the Dora Maira
178 Massif in western Alps (Italy), a slice of continental crust that experienced subduction to ultra-
179 high pressure conditions (P= 3.5 GPa, T= 750°C) (e.g., Ferrando et al., 2009, and references
180 therein). Abundant aqueous fluid inclusions have been previously described in pyrope from these
181 lithologies (Ferrando et al., 2009; Philippot and Selverstone, 1991).

182

183 2. Analytical Methods

184

185 Raman spectra of minerals and fluid inclusions containing C and H were acquired with a
186 Labram microspectrometer (HORIBA Jobin Yvon) at the University of Siena. A polarized 514.5
187 nm water-cooled Ar-ion laser was used as the excitation source. The measured laser power was
188 300-500 mW at the source, and about 80% less at the sample surface. Raman spectra were
189 collected through an OLYMPUS 100x objective (0.9 numerical aperture: excitation spot 1x1x5

190 μm in volume) for an acquisition time variable from 30 s to 180 s for each spectrum, and 1 to 10
191 accumulations. The slit width was set at 100 μm , and the corresponding spectral resolution was
192 1.5 cm^{-1} . Frequency wavenumbers of the Raman modes in the region 0-1800 cm^{-1} were
193 calibrated daily by the position of the diamond peak at 1331.7 cm^{-1} . Peak assignment of solid,
194 gaseous, and liquid phases was done by comparison with our reference library and database of
195 Raman spectra (http://www.dst.unisi.it/geofluids/raman/spectrum_frame.htm; Frezzotti et al.,
196 2012).

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

205 To reveal water diffusion from fluid inclusions into the structure of surrounding minerals,
206 we mapped the distribution -and concentrations of structurally_bound hydrogen in nominally
207 anhydrous minerals by synchrotron based FT-IR microspectroscopy. We selected those mantle
208 minerals where liquid H_2O was proven in fluid inclusions: olivine and pyroxenes from Ethiopian
209 peridotite xenoliths (Frezzotti et al., 2010), and garnet from Dora Maira whiteschists (Ferrando
210 et al., 2009). Analyses were performed by Fourier transform infrared (FT-IR) microspectroscopy
211 at the infrared beam-line SISSI (Source for Imaging and Spectroscopic Studies in the Infrared)
212 operating at the synchrotron laboratory ELETTRA in Trieste. Spectra were collected on a FTIR
213 spectrometer (Bruker IFS66/v) fitted with a Hyperion IR microscopy with a liquid-nitrogen-
214 cooled HgCdTe (MCT) detector. Infrared microscopy was performed on an infrared microscopy
215 system (Bruker) with a 16 \times magnification infrared objective. Spectra were collected at resolution

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216 of 4 cm^{-1} and signal averaged for 128 scans on each data collection. Background spectra were
217 recorded in air. For IR imaging studies, we used double-polished thick sections of xenoliths of
218 known thickness. The spectral images were collected scanning areas of variable sizes (200-450
219 μm -long and 200-450 μm -wide), following a regular grid of square-aperture dimension of 20 μm
220 equidistant by 20 μm in both directions (i.e., totals of 100-400 spectra), using a computer-
221 controlled automated X-Y mapping stage. Interpretation of unpolarized spectra of H_2O followed
222 the classical group frequency approach in which absorption bands are assigned to specific
223 vibrational modes. OH concentrations in mineral phases were estimated from the integrated
224 absorbance using the Beer-Lambert law (Paterson, 1982). Experimentally determined calibration
225 constants for orthopyroxene are from Bell et al. (1995), and for olivine are from Bell et al.
226 (2003). Since unpolarized FT-IR H_2O measurements are affected by large errors (30-50 %; cf.,
227 Demouchy et al., 2006), and imaging revealed H variations with position within single minerals,
228 measured water contents are reported in intervals of tens of ppm, emphasizing the relative
229 variations with distribution within single grains. Note that, liquid H_2O and/or hydrous minerals
230 in fluid inclusions were also suggested by FT-IR absorption bands. However, spectra are not
231 reported in the present paper, since we consider FT-IR microspectroscopy a less reliable
232 diagnostic technique than Raman, because of its poorer resolution, and absence of confocality.

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

238

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240

241

242 **3. Results**

243

244 Water in CO₂-rich fluid inclusions is traditionally revealed by optical studies, although
245 identification may be difficult in dense and often colored mantle minerals (cf., Roedder, 1972).
246 Water can be detected simply by using Raman and FT-IR spectroscopic techniques (cf., Frezzotti
247 and Peccerillo, 2007; Hidas et al., 2010; McMillan et al., 1996, and references therein). Results
248 are given in Table 2 and discussed in the following sections. Note that the potential of Raman
249 microspectroscopy for identifying water in mantle fluid inclusions has been known since the 80's
250 (e.g., Pasteris and Wanamaker, 1988). However, researchers failed to detect H₂O in fluid
251 inclusions at that time, probably because of the non-confocality and lower sensitivity of old
252 instruments.

253 4.1 Uncovering aqueous fluids inside inclusions: Raman spectroscopy and EDAX-EDS analyses

254 In almost all studied fluid inclusions H₂O is not visible. One exception is represented by a
255 few relatively-large fluid inclusions (> 20 – 30 μm) in orthopyroxene of spinel lherzolites from
256 the Ethiopian plateau, where thin (≤ 1 μm) liquid water films were recognized. In these
257 inclusions, presence of H₂O was confirmed by clathrates melting during microthermometric
258 studies at low temperatures (Table 2).

259 Raman microspectroscopy revealed the presence of liquid water in a minority of optically
260 “pure” CO₂ fluid inclusions (10-30 μm in size), for which pyroxenes were the enclosing
261 minerals, and a hydrous nature was recognized for the host mantle peridotites (e.g., Ethiopian
262 plateau and Central Italy; Table 2 and Fig. 1a). For example, a Raman spectrum of liquid H₂O is
263 reported in Figure 1b. The characterizing feature consists of a broad band centered
264 approximately at 3400-3450 cm⁻¹ in the OH stretching region from 2900 to 3800 cm⁻¹. In those
265 fluid inclusions of less than 5 μm in size, a water film rimming the CO₂ does not generate a
266 discernible liquid H₂O Raman spectrum. However, Raman detection of H₂O was possible also in

267 these cases by spectra of isolated H₂O molecules dissolved in the CO₂ fluid (Table 2; Frezzotti
268 and Peccerillo, 2007).

269 A coat of hydrous silicates and/or carbonates distributed along the rims of fluid inclusions
270 was more commonly identified in place of molecular H₂O (Table 2; Fig 2 a-d). Talc (Tlc) was
271 recognized by its band distribution in the OH⁻ region at 3677 cm⁻¹ (Fig. 2f). More rarely, band
272 distribution at 3450, 3638, 3673 cm⁻¹ was observed, which corresponds to Mg-chlorite
273 (Mg₅AlSi₃AlO₁₀(OH)₈; not shown). Magnesite (Mgs) was identified by its diagnostic Raman
274 modes at 1092, 738, and 328 cm⁻¹ (Fig. 2e). Whereas the presence of carbonates in fluid
275 inclusions was revealed by optical microscopy (Fig. 2c and d), talc and chlorite were generally
276 overlooked. The type and amount of minerals lining CO₂-rich inclusions depend mainly on the
277 nature of the surrounding mineral (Table 2). In olivine, hydrous silicates and carbonates are
278 common phases (Fig. 2b and c), and in a few cases completely fill the inclusions, without any
279 fluid left (Fig. 2d). Conversely, in orthopyroxene and clinopyroxene, while carbonates are
280 common, hydrous silicate minerals are less frequent (Fig. 2a).

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

288 In clinopyroxene from hydrous peridotites (Table 1), EDS-EDAX analyses showed that
289 CO₂-rich inclusions occur in contact with a euhedral hydrous mineral, similar in size and
290 chemically identical to the metasomatic phase present in the rocks: pargasite in peridotites from
291 the Ethiopian plateau (Fig. 4a and c), and phlogopite in peridotites from Sardinia (Italy) (Fig. 4b
292 and d).

293

294 4.2 Mapping water diffusion from fluid inclusions: FT-IR spectroscopy

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

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

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

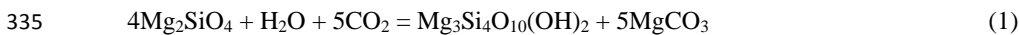
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319 **5 Discussion**

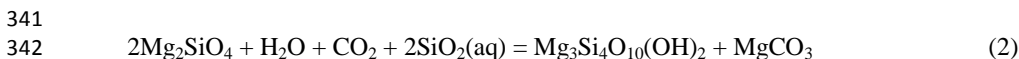
320 *5.1 There was water in fluid inclusions formed at shallow-mantle depths*

321 The present study highlights significant dehydration of shallow-mantle fluids after trapping as
322 inclusions. Diffusive loss of H₂O due to re-equilibration between the inclusion and host is
323 demonstrated by the strong FT-IR absorbance peak of water migration in the host nominally
324 anhydrous mantle minerals. Transport of water could have occurred under conditions of
325 differential pressures and fluid fugacity at high *P* and *T* through lattice defects and
326 microfractures. A high-concentration of dislocations around fluid inclusions was previously
327 reported in olivine from Canary Islands peridotites, and was proposed to be the main mechanism
328 for molecular fluid loss (Viti and Frezzotti, 2000; 2001). This diffusion-scenario is conceivable
329 considering the extremely fast diffusion of H in olivine (Mackwell and Kohlstedt, 1990), and
330 reinforces models proposed for selective H₂O loss from CO₂-H₂O inclusions in quartz (Bakker
331 and Jansen, 1991; Romer et al., 2006; Sterner and Bodnar, 1989; Watson and Brenan, 1987).

332 Further, dehydration of mantle fluids is induced by reactions between residual H₂O fluids in
333 the inclusions and the surrounding minerals. In magnesian olivine, the association of talc and
334 magnesite may form at low *T* and *P* through the following reaction:



336 However, talc and magnesite relative volumes observed in fluid inclusions (Fig. 3a) suggest that
337 sub-equal molar amounts of these two phases were produced during the reaction, given that the
338 molecular weight of talc is about five times that of magnesite (379 vs. 84), for similar densities
339 (2.78 vs. 3.01 g/cm³). Relative proportions of talc and magnesite can be greatly modified if H₂O-
340 CO₂ fluids contained SiO₂ in solution:

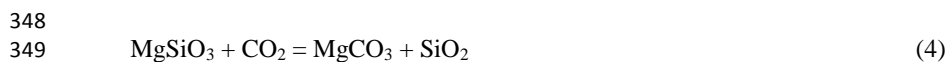


343 In magnesian orthopyroxene, formation of talc and magnesite can be described by a reaction:



345
346 However, while magnesite represents a common phase in fluid inclusions, talc is more rare.

347 It is thus possible that a second reaction such as:



350
351 might have occurred between H_2O - CO_2 fluids of variable $X_{\text{H}_2\text{O}}$ and surrounding orthopyroxene.

352 In contrast, fluid inclusions in clinopyroxene do not seem to contain or have contained H_2O .
353 Talc and magnesite are rare, and FT-IR absorption maps do not show significant water
354 enrichments. This result is surprising, given that the capacity of clinopyroxene to store H_2O
355 greatly exceeds that of olivine at upper mantle pressures (Aubaud et al, 2004). Although we may
356 have overlooked some processes, as the studied clinopyroxene is from hydrous peridotites where
357 metasomatic amphibole or phlogopite are present, our preferred explanation for the analytical
358 data is that reaction of the hydrous fluid occurred along microfractures at the infiltration stage,
359 prior to inclusion formation. Hydration of clinopyroxene during microfracture healing is
360 suggested by formation of tiny pargasite (or phlogopite) grains, occurring with CO_2 fluid
361 inclusions along the same microfracture (Fig. 4). In olivine and orthopyroxene, similar hydration
362 reactions are inhibited, since they occur at lower temperatures below most mantle geotherms (see
363 also section 5.2), and hydrous mantle fluids are trapped inside inclusions. Interestingly, Lamb et
364 al. (1987) proposed a similar evolution to explain selective CO_2 enrichments observed in fluid
365 inclusions of some high-grade metamorphic rocks.

366

367 5.2 Amounts of water in shallow-mantle fluids

368 A critical question to petrological and geophysical studies is how much water was originally
369 present in shallow-mantle fluids. This issue can be investigated by modeling the reactions
370 between H_2O - CO_2 fluid inclusions and surrounding magnesian orthopyroxene ($\text{Mg}/\text{Mg}+\text{Fe}=0.9$)

371 in peridotites. For magnesian olivine, similar reactions cannot be modeled since they require
372 SiO_2 in the fluid (cf., reaction 2 in 5.1). Figure 7 shows T - $X_{\text{H}_2\text{O}}$ phase diagrams for the MFSHC
373 model system at different pressures. The model reactions can be used to simulate the chemical
374 re-equilibrations between aqueous-carbonic fluids with different $X_{\text{H}_2\text{O}}$ in inclusions and
375 surrounding orthopyroxene. These diagrams show that the minimum $X_{\text{H}_2\text{O}}$ necessary to induce
376 hydration reactions between fluid inclusions and surrounding minerals increases with increasing
377 fluid pressure. If we consider the formation of talc inside a fluid inclusion in orthopyroxene, at 1
378 GPa, the minimum $X_{\text{H}_2\text{O}}$ is 0.25 (see invariant point 1 in Fig. 7b), while at 0.5 GPa, it decreases
379 to $X_{\text{H}_2\text{O}}=0.1$ (invariant point 1 in Fig. 7c). The maximum $X_{\text{H}_2\text{O}}$ should not exceed 0.5 regardless
380 of pressure, since ensuing reactions would consume equal amounts of H_2O and CO_2 , whereas
381 observed fluid inclusions have CO_2 -rich compositions. From figure 7, it is also evident that
382 reactions between H_2O - CO_2 fluid inclusions and the surrounding minerals cannot be a mantle
383 process, as talc and/or magnesite only forms as temperatures decrease below about 700-600°C
384 for variable pressures. We propose that eruption provides the conditions to induce reactions. In
385 explosive eruptions, temperatures of xenoliths fall below 600°C over 5-10 sec. of ballistic
386 transport through the air (Shaw, 2009). Even in slower-cooling lavas, xenoliths take only a few
387 hours to reach the same temperatures.

388 A strong dependency on pressure for hydrous fluid inclusion evolution is illustrated in Figure
389 8. Consider a dense CO_2 - H_2O fluid inclusion with $X_{\text{H}_2\text{O}}=0.3$ in orthopyroxene formed at 1.5 GPa
390 and 1000°C in a mantle peridotite. When this inclusion ascends rapidly and adiabatically in a
391 xenolith within the host magma, it will effectively become overpressurized (path a in Fig. 8). If
392 decrepitation does not occur, it arrives at the surface, and subsequent syn-, and post-eruptive
393 decrease of temperature will cool the fluid in the inclusion along an isochore (path b in Fig. 8).
394 At temperatures below approximately 700°C, CO_2 - H_2O fluid reaction with surrounding minerals
395 promotes the formation of magnesite in inclusions, but not hydrous phases (i.e., reaction 4 in
396 5.1). As far as a fluid inclusion remains overpressurized during adiabatic ascent and cooling,

397 hydrous phases cannot form. When the same fluid inclusion decrepitates during ascent, so that
398 fluid density resets to a lower value corresponding, for example, to $P < 1\text{GPa}$ (below point 1 in
399 Fig. 8), syneruptive cooling along isochore (path c in Fig. 8) would make the $\text{CO}_2\text{-H}_2\text{O}$ fluids in
400 the inclusion to react to form talc + magnesite (reaction 3 in 5.1).

401 In summary, thermodynamic modeling suggests that up to 50 mole % water should have been
402 present in fluid inclusions formed at mantle depths in order to drive the observed reactions in
403 orthopyroxene. Petrogenetic grids also show that syneruptive cooling in host peridotite xenoliths
404 promotes fluid reactions with surrounding minerals. Lower overpressures in the fluid inclusion
405 require a lower minimum water amount in the fluid in order for hydration reactions to take place.
406 It appears reasonable to conclude that hydration reactions associated with diffusive water loss
407 reset fluid inclusions to the minimum concentration of H_2O and produce a dehydration trend
408 which may result in the “pure CO_2 ” inclusions often described in mantle minerals. It is
409 noteworthy to recall that any geobarometric data derived from similar CO_2 -rich inclusions could
410 result in underestimates, since CO_2 -rich fluids would have residual composition and density
411 considerably lower than that of the original mantle fluids at the time of entrapment.

412

413 5.3 Reevaluation of shallow-mantle fluid composition

414 In the absence of pristine inclusions in mantle minerals, an accurate characterization of the
415 chemistry of the aqueous fluid component is complicated. Even so, the identity of minerals
416 precipitating inside fluid inclusions through reactions with surrounding minerals gives
417 information on the nature of species in solution. Ubiquitous talc forming through fluid reaction
418 with surrounding host phases indicates Si as a major solute component (cf., reactions 2 and 3 in
419 5.1). Additionally, relevant amounts of Cl, S, Ca, K, and Na are revealed by chlorides and
420 gypsum precipitated in inclusions on cooling. Interestingly, K seems to be present in relatively
421 higher amounts than Na. Sulfur has been identified either as hydrogen sulfide gas (H_2S),
422 elemental sulfur (S_8), or as sulfate ions (hydrated form of SO_3) (Table1) depending on the

423 oxidation state of the fluid, and indeed sulfur appears to bear a major control over the oxidation
424 state. The sulfate ions detected in some fluid inclusions are a real feature, since, eventual
425 postentrapment fluid inclusion redox-reactions would tend to reduce sulfur (Grishina et al.,
426 1992).

427 The model composition of saline multicomponent mantle fluids that emerges from the present
428 study is in agreement with formation of Cl-rich hydrous metasomatic phases and with extreme
429 LILE enrichments in the studied peridotites (cf., section 2). In addition, the applicability of new
430 chemical data to natural mantle fluids is supported by studies on major element solubility at high
431 *P* and *T*. Experimental data up to 3 GPa and 1300°C indicate alkalis as the most soluble species
432 in aqueous fluids, followed by Cl, Si, and Ca, while Mg and Fe are relatively less soluble
433 (Brenan et al., 1995; Dvir et al., 2011; Egglar, 1987; Kawamoto et al., 2004; Manning, 2004;
434 Nakamura and Kushiro, 1974; Newton and Manning, 2002; Stalder et al., 2001). For example,
435 Nakamura and Kushiro (1974) estimated that 20 wt. % silica is dissolved in H₂O fluids
436 coexisting with mantle enstatite at 1.5 GPa and 1280°C. The presence of CO₂ in the fluid
437 strongly depresses the solubility of silica, while the presence of chlorine has the opposite effect
438 (cf., Newton and Manning, 2010).

439 Previous direct measurements indicated that 10-14 wt% solutes (in NaCl equivalent) are
440 present in hydrous fluid inclusions from the Ethiopian plateau (see section 2). Measured solute
441 concentrations are in agreement with 2-5 wt% Cl (or 3.5-9 wt. % in NaCl equivalent) predicted
442 for mantle fluids (Burgess and Turner, 1995), and with 6-10 wt % solutes measured in H₂O-rich
443 subduction fluids (1-2 GPa; Manning, 2004). The total fluid solute content cannot have been
444 extreme in order to trap homogeneous fluids in inclusions (Figs. 1 and 2). High-salinity aqueous
445 fluids, having a large immiscibility solvus in the CO₂-H₂O-NaCl system, would have been
446 immiscible with CO₂ at the considered mantle *P-T* conditions (Touret, 1992; 2009). Phase
447 separation (into L+V) would have formed distinct CO₂-rich and saline-aqueous fluid inclusions
448 in mantle minerals, which have not been observed. Based on these observations, the concentrated

449 brines ($\text{NaCl} \geq 50$ wt %; Scambelluri et al., 1997) described in fluid inclusions of some
450 peridotites from subduction settings are likely to reflect the evolution of multicomponent fluids
451 towards increasing solute/ H_2O ratios either by decompression-induced phase separation in the
452 CO_2 - H_2O -salt fluid system, or by postentrapment inclusion “dehydration” trends.

453

454 5.4 Origin of water and chlorine in shallow-mantle fluids

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

464 Our data raise the question of the origin of aqueo-carbonic fluids carrying significant amounts
465 of Cl in the lithosphere within the context of intraplate and extensional mantle settings (e.g.,
466 Ethiopia, and Hawaii) (Le Roux et al., 2006; Michael and Schilling, 1989; Seaman et al., 2004;
467 Stolper et al., 2004). In the east African lithosphere, evidence for mantle metasomatism driven
468 by Cl-bearing hydrous fluids is consistently reported from several xenolith localities and
469 supposed to have occurred during the early stages of mantle upwelling. The Cl-pargasite bearing
470 lithosphere under the Ethiopian plateau is considered to have been modally metasomatized by
471 CO_2 -brine fluids, probably derived by degassing of deep carbonate rich melts during early stages
472 of upwelling of the Afar mantle zone (Frezzotti et al., 2010). Additionally, Cl-rich pargasite in
473 spinel lherzolites of Zabargad Island is interpreted to have formed just before the early rifting
474 phase of the Red Sea (Agrinier et al., 1993). In a similar way, the growth of amphibole \pm Cl-

475 apatite in spinel peridotites from Yemen has been proposed to have been induced by the influx of
476 carbonatitic melts and hydrous fluids from the Afar plume during the Oligocene (Baker et al.,
477 1998). At Hawaii, Iceland, and Azores, Cl-enrichment in the lithosphere is indicated by the high
478 Cl/F ratios of melt inclusions in OIB (e.g., Dixon et al., 2008; Le Roux et al., 2006; Michael and
479 Schilling, 1989; Seaman et al., 2004; Stolper et al., 2004).

480 There should be other water and Cl-sources besides active subduction. Evidence for hydrous
481 mantle fluids away from subduction zones has been obtained in cratonic areas by fluid inclusions
482 in fibrous diamonds, where fluids consist of three main components: a carbonate melt, a silicate
483 melt, and a hydro-saline fluid (e.g., Izraeli et al., 2001; Klein-BenDavid et al., 2004; 2007;
484 Kopylova et al., 2010; Navon et al., 1988). The hydrous fluid component is enriched in SiO₂,
485 Al₂O₃, halides, and alkalis (mainly K), similar to shallower hydrous fluids reported by this study.
486 The total solute content is, however, considerably higher in diamond fluids (e.g., Cl up to ca. 35
487 wt. %), possibly reflecting the increase of elements solubility at greater *P* and *T* ($P \geq 4\text{-}5$ GPa;
488 e.g., supercritical fluid phases; Bureau and Keppler, 1999; Kawamoto et al., 2004; Kessel et al.,
489 2005; Manning, 2004). In diamonds, continuous compositional variations of fluid inclusions are
490 observed, suggesting that all components might be genetically related, most likely evolved from
491 a “primitive” carbonate-rich melt (cf., Klein-BenDavid et al., 2004, and references therein).
492 Recent experimental evidence shows that immiscibility processes in this silicate–carbonate–H₂O
493 system facilitate the chlorine enrichment of the carbonate melt or of the aqueous fluid, not only
494 at high pressures in the diamond stability field, but also at lithospheric pressures (Litasov and
495 Ohtani, 2009; Litasov et al., 2011; Safonov, 2011).

496 It is conceivable to suppose that Cl-bearing hydrous shallow mantle fluids might have been
497 formed through hydro-saline carbonate melts. As mentioned above, the model composition of
498 hydrous shallow mantle fluids in spinel peridotites is similar to that of the aqueous fluid
499 component trapped deeper, in diamonds. Further comparisons are difficult because of the limited
500 data. Fluxes of CO₂–H₂O and Cl in the lithosphere could have been generated by degassing of

501 upwelling carbonate-rich melts at pressures below the carbonate-stability field (2–2.5 GPa;
502 Dobson et al., 1996; Hammouda and Laporte, 2000). Since fluid data from mantle rocks in
503 intraplate and extensional tectonic settings are limited, it is not known whether carbonate-melt
504 degassing may be the main source of lithospheric hydrous fluids, or some other mechanisms,
505 such as silicate melt – fluid immiscibility, have to be invoked. In any case, the deep association
506 of CO₂, H₂O, carbonates, and diamonds preserved in fluid inclusions of Hawaiian garnet
507 pyroxenites (Frezzotti and Peccerillo, 2007) was interpreted to have caught this process in the act.
508

509 **6. Conclusions**

510

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

520 Although shallow mantle fluids are generally dominated by CO₂, constraints from
521 thermodynamic modeling in the MFSHC system suggest that up to 50 mole % H₂O could be
522 present. Water activity ($a_{\text{H}_2\text{O}}$) is expected to be low (probably < 0.4), in agreement with the
523 anhydrous nature of many peridotite xenoliths. However, the existence of a hydrous fluid
524 component will influence the physical and chemical evolution of the shallow mantle. Presence of
525 H₂O and solutes makes migration of fluids more effective (Mibe et al., 1998, 1999; 2002;
526 Watson and Brenan, 1987). Moreover, the solute content in such hydrous fluids will affect

527 transport and partitioning of elements inducing metasomatism in mantle rocks (Ayers, 1998;
528 Keppler, 1996; Kessel et al., 2005; Konrad-Schmolke et al., 2011).

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

534

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543

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Captions to Figures

858

859 Fig. 1 - Raman detection of optically hidden liquid water in fluid inclusions. a) Trail of fluid
860 inclusions in orthopyroxene. White asterisks indicate those fluid inclusions where liquid H₂O
861 was detected by Raman spectroscopy. b) Raman spectrum of liquid H₂O rimming CO₂ in a fluid
862 inclusion in Fig. 2a.

863

864 Fig. 2 - Different extents of fluid inclusion-host reactions as detected by Raman
865 microspectroscopy. Inclusions show textural evidence for an increasing reaction degree with the
866 enclosing mineral going from microphotographs a-b, to c and d. a) Decrepitated high-density
867 (monophase) CO₂ fluid inclusion containing magnesite (Mgs) in orthopyroxene. b) Magnesite
868 (Mgs) and talc (Tlc) in apparently preserved high density (monophase) CO₂ fluid inclusions
869 distributed along a trail in olivine. c) Decrepitated and reacted fluid inclusion in olivine.
870 Inclusion contains two phase (liquid + vapor) CO₂, Mgs, and Tlc. d) Decrepitated and reacted
871 fluid inclusion in olivine. The inclusion is filled by aggregates of Tlc and Mgs, with no visible
872 fluid left. e) Raman modes of magnesite inside fluid inclusions. Unlabelled peaks refer to
873 enclosing olivine. f) OH⁻ Raman modes of talc recorded inside fluid inclusions.

874

875 Fig. 3 - EDS-EDAX and Raman analyses in open fluid inclusions. a) Electron microphotograph
876 of an open inclusion in olivine. Talc (Tlc) and magnesite (Mgs) coat the inclusion walls. b)
877 Electron microphotograph of an open fluid inclusion in orthopyroxene. Tlc is distributed along
878 the inclusion walls. A thin microcrystalline coating of gypsum, KCl, NaCl, SiO₂, and Fe-Al
879 oxides is observed on talc crystals (inset). c) Qualitative EDS-EDAX chemical analysis of the
880 coating shown in Fig. 3b (inset image). d) Main Raman modes of gypsum inside the fluid
881 inclusion in Fig. 3b. Unlabelled peaks refer to enclosing orthopyroxene. e) OH⁻ Raman modes of

882 gypsum. Raman spectra in Fig. 3d and e were collected in the same area of EDS-EDAX analysis
883 (inset image in 3b).

884

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

893

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

902

903 Fig. 6 - Synchrotron FT-IR imaging of water distribution in olivine. Microphotograph of
904 investigated area in olivine containing several fluid inclusions. b) Absorbance map in the 3000–
905 3600 cm^{-1} region and calculated water contents in olivine (ppm). The color scale is proportional
906 to OH^- enrichment (increasing from blue to pink). Measured water contents are drawn with a
907 precision of 10's of ppm. c) Qualitative distribution map of OH absorbance for talc and

908 serpentine in the 3600–3800 cm^{-1} region, which allows to qualify hydrated phases in olivine.

909 a.u.: arbitrary units.

910

911 Fig. 7 – T - $X_{\text{H}_2\text{O}}$ petrogenetic grids at 1.5 GPa, 1.0 GPa, 0.5 GPa, and 0.1 GPa in the MgO-FeO-
912 SiO₂-H₂O-CO₂ system, calculated with En and Fo compositions at #mg = 0.9, calculated with the
913 thermodynamic approach of Connolly (1990). White dots are the invariant points. Black solid
914 curves highlight possible reactions between H₂O-CO₂ fluids trapped in inclusions and the
915 surrounding magnesian orthopyroxene. All reaction equations are written such that the high- X_{CO_2}
916 assemblage is on the right side. The occurrence of talc as product of reactions depends on fluid
917 pressure and on $X_{\text{H}_2\text{O}}$ (invariant point 1), see 5.2.

918

919 Fig. 8 - P - T petrogenetic grid at $X_{\text{H}_2\text{O}} = 0.3$ in the MgO-FeO-SiO₂-H₂O-CO₂ system, calculated
920 with En and Fo compositions at #mg = 0.9. White dots are the invariant points. Black thick solid
921 curves highlight possible reactions between H₂O-CO₂ fluids trapped in inclusions and the
922 surrounding orthopyroxene. All reaction equations are written such that the low- $X_{\text{H}_2\text{O}}$
923 assemblage is on the right side. The oval and the star indicate the P - T conditions of fluid
924 inclusion trapping and fluid inclusion decrepitation, respectively. The thick black arrow (a)
925 represents the P - T path of a mantle xenolith within the host lava. The dashed grey lines represent
926 isochores of preserved (b), and decrepitated (c) fluid inclusions. The two thin black arrows
927 represent the P - T paths of preserved (high density, isochore b), and decrepitated (low density,
928 isochore c) fluid inclusions. As evident from the grid, syn-, and post-eruptive reactions between
929 fluid inclusions and surrounding orthopyroxene can produce hydrous minerals (talc) only in low-
930 density fluid inclusions (c).

*Highlights

- 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

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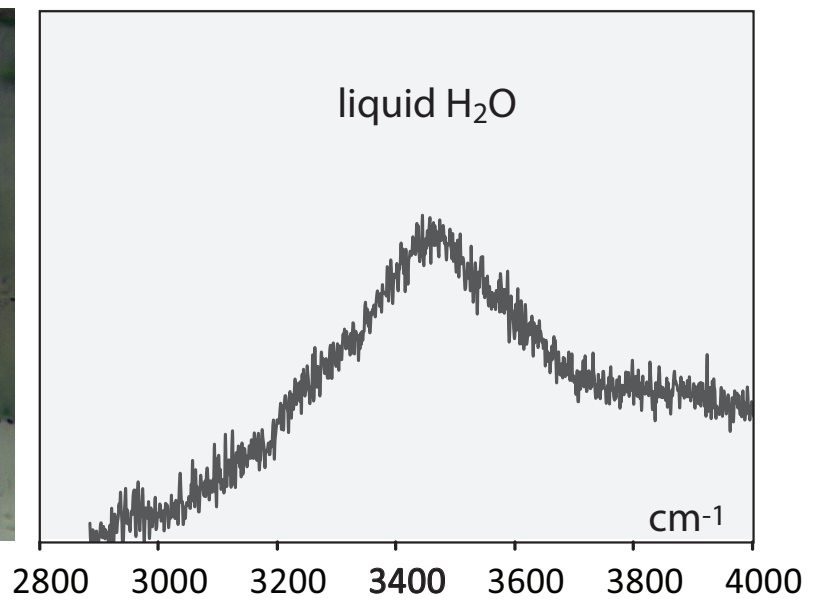
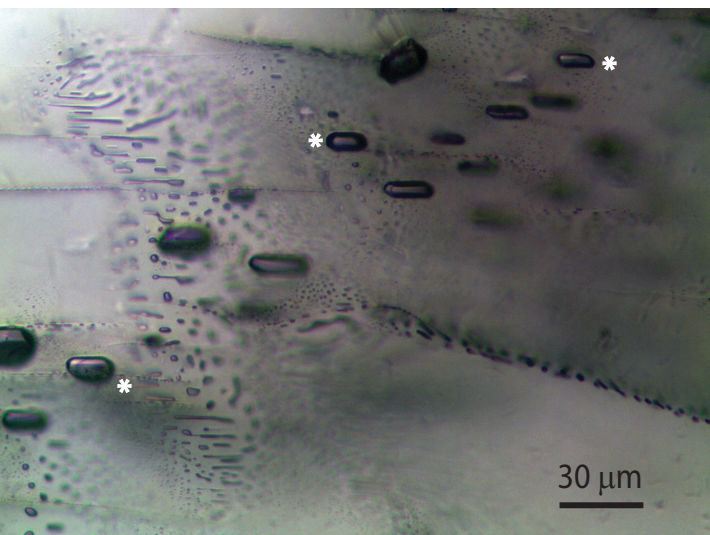


Figure 2
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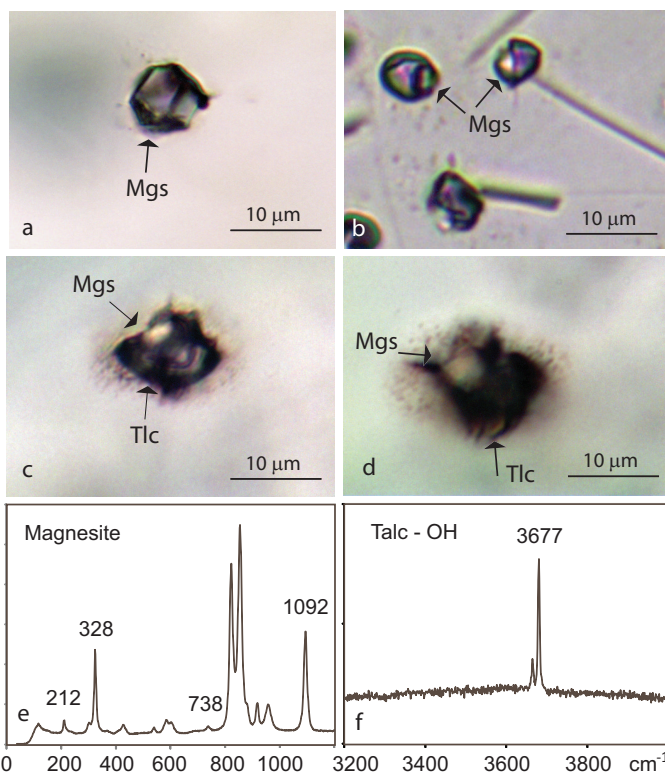


Figure 3
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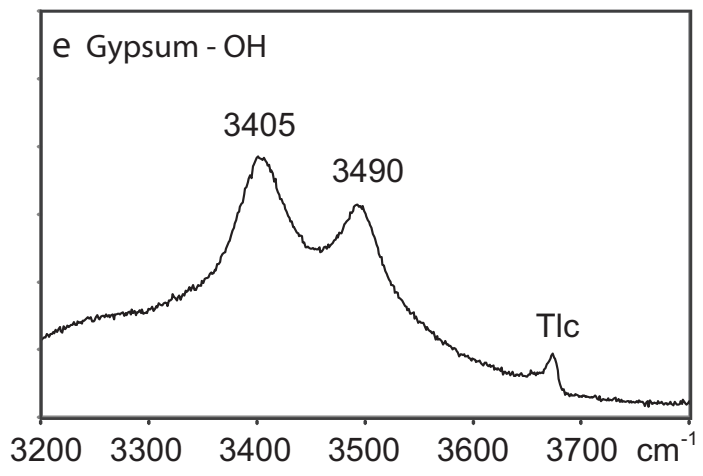
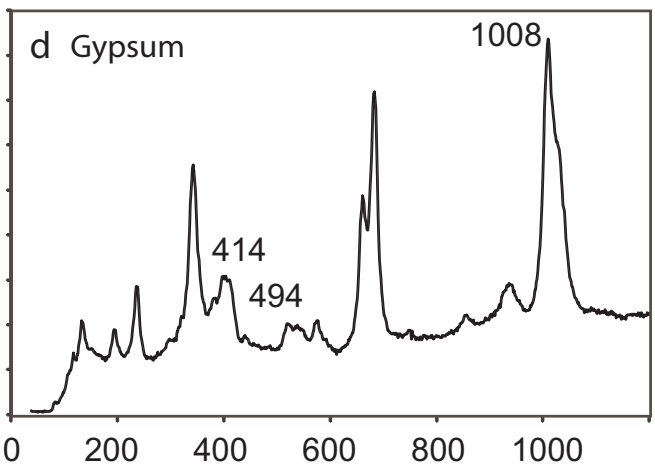
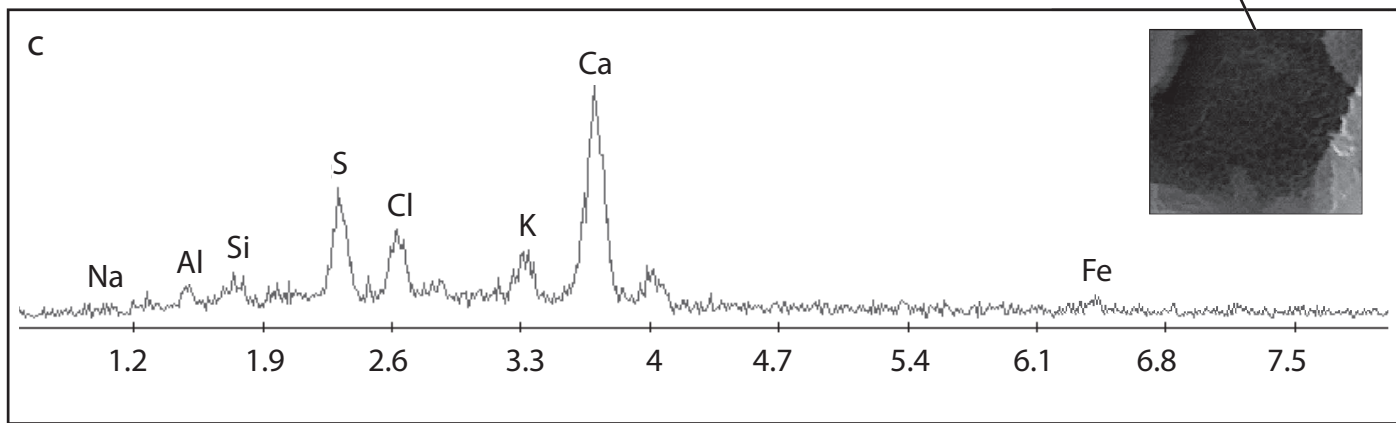
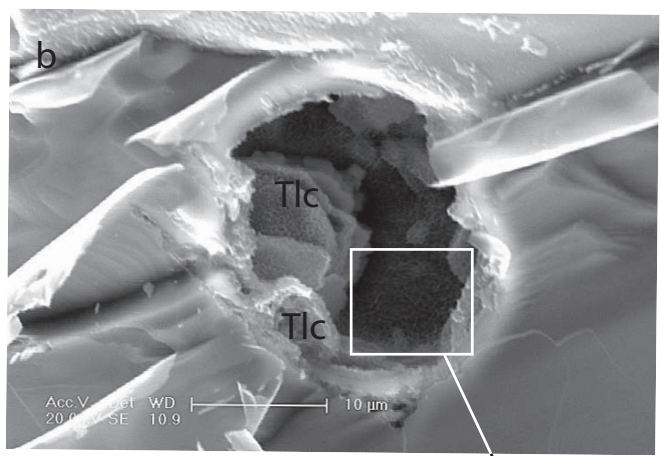
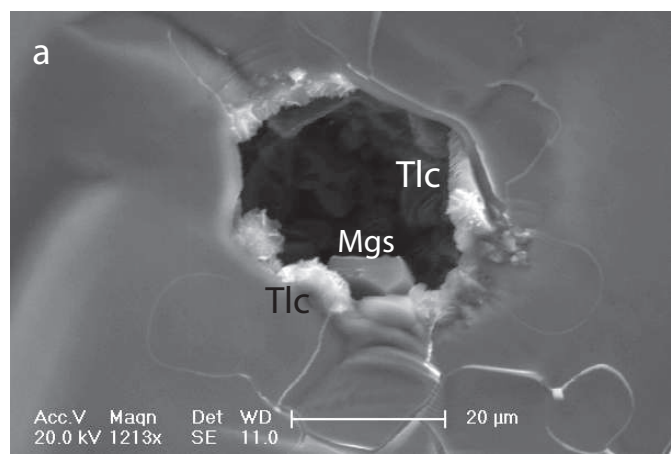


Figure 4
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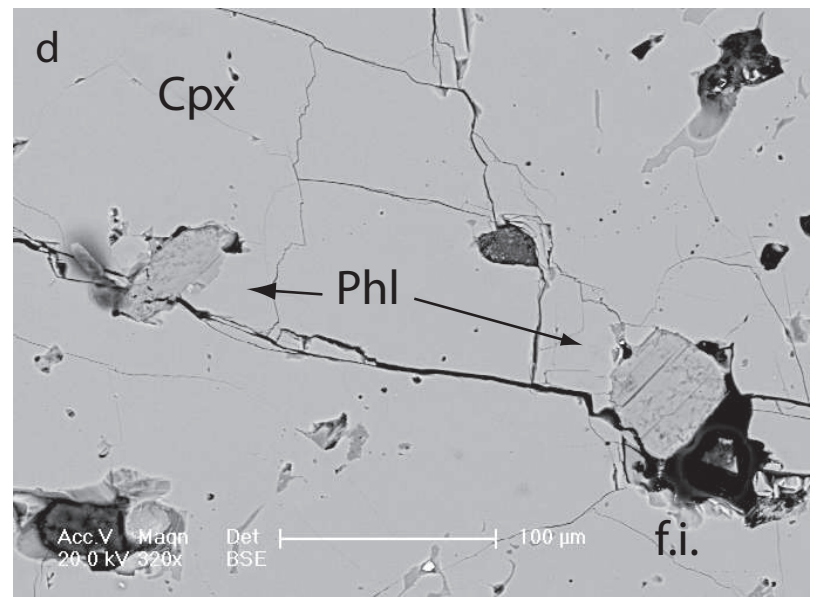
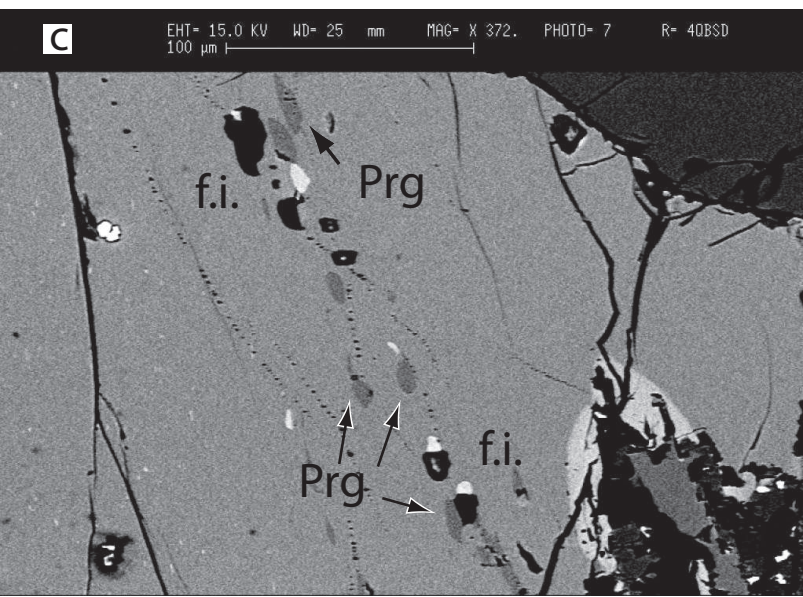
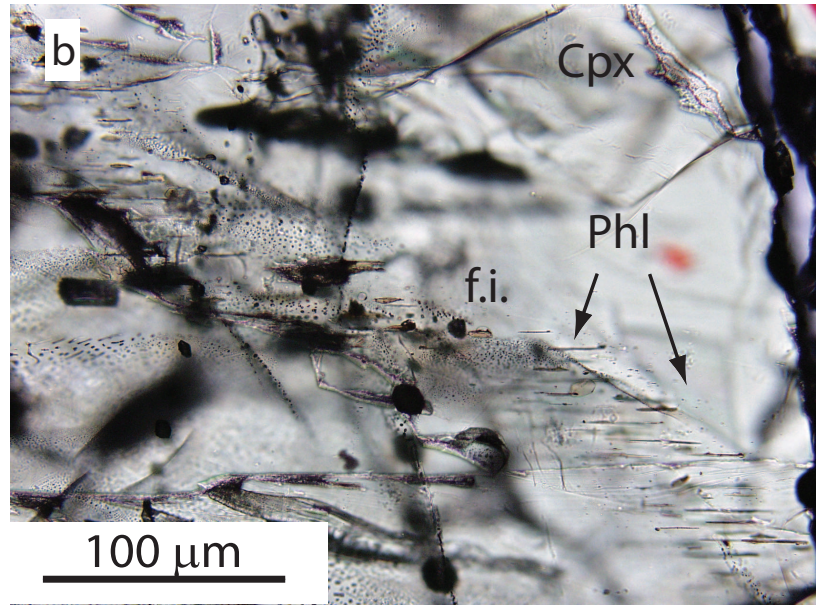
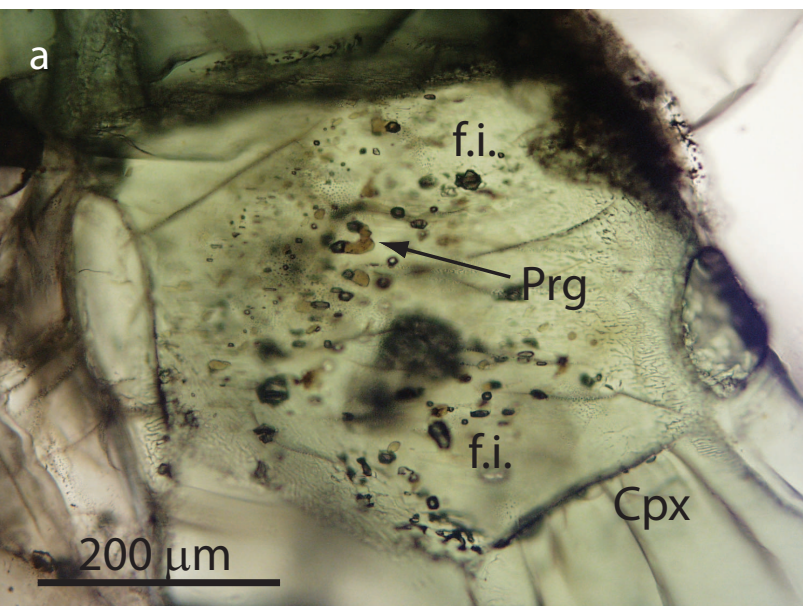
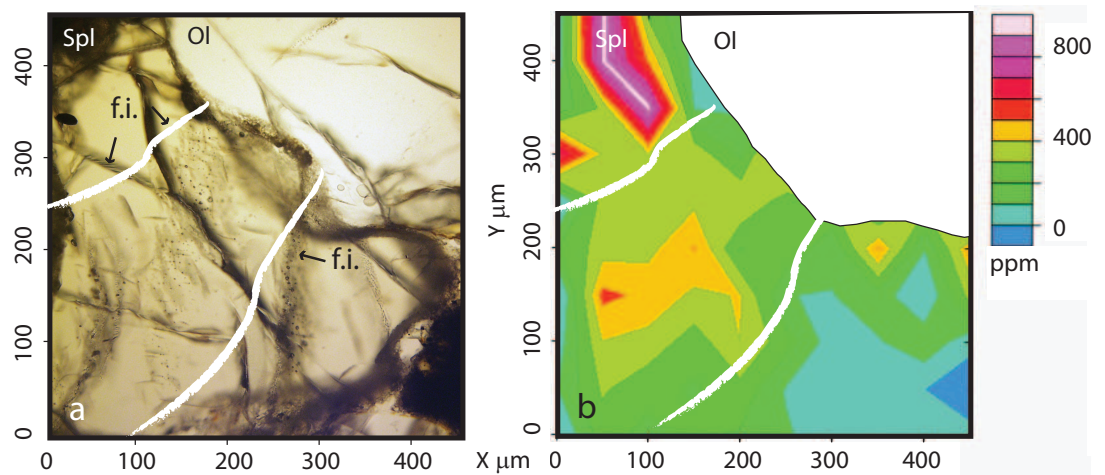


Figure 5

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H₂O content in orthopyroxene



H₂O content in garnet

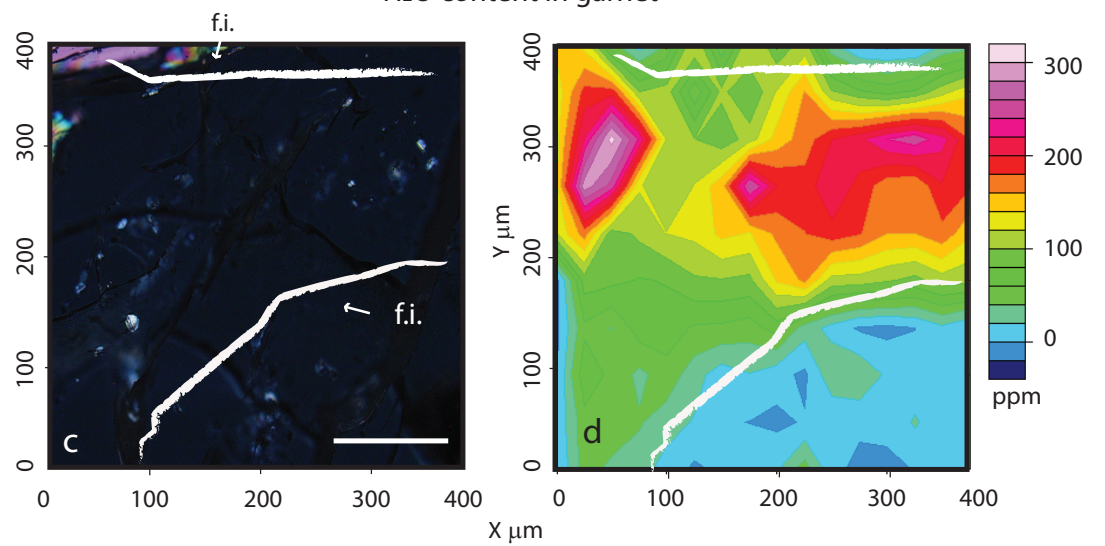


Figure 6

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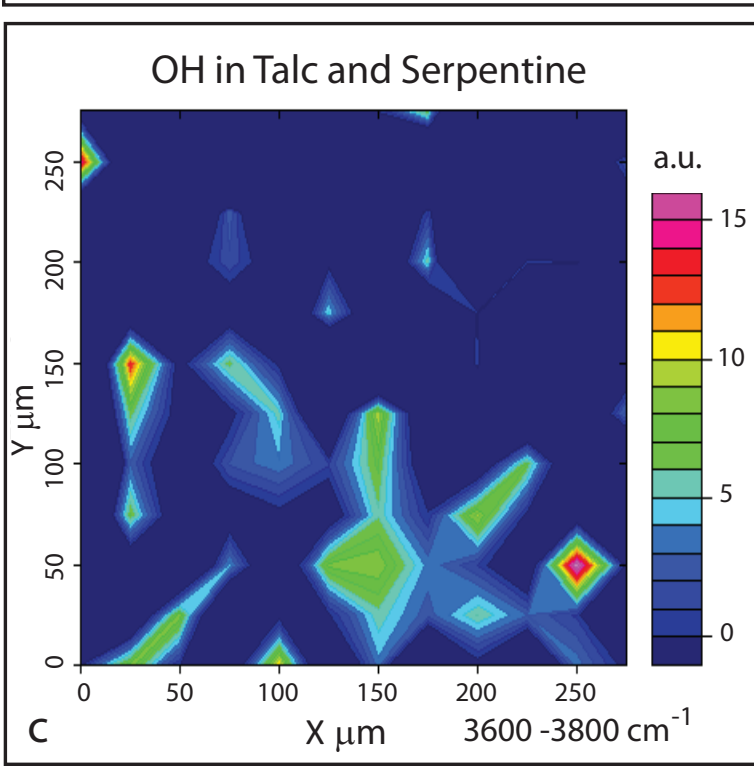
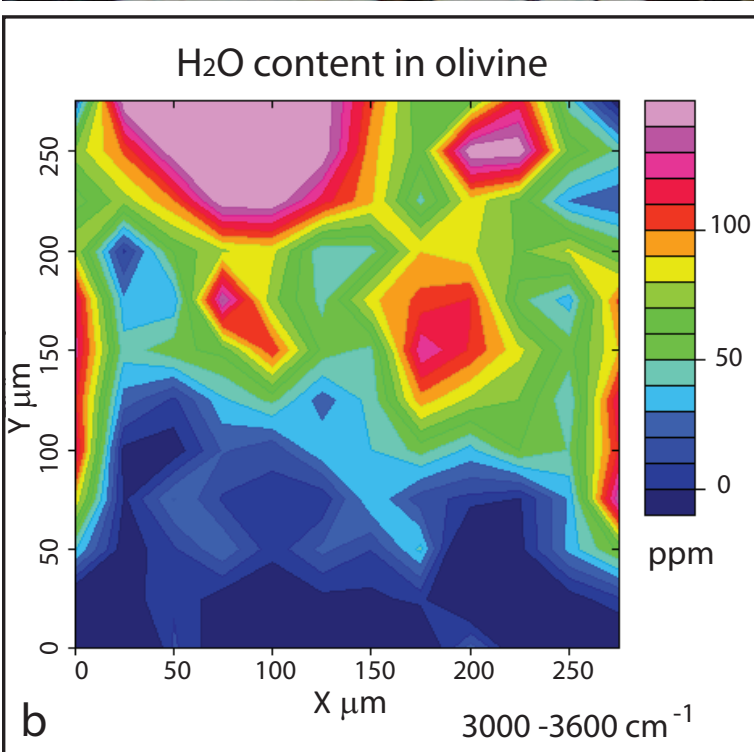
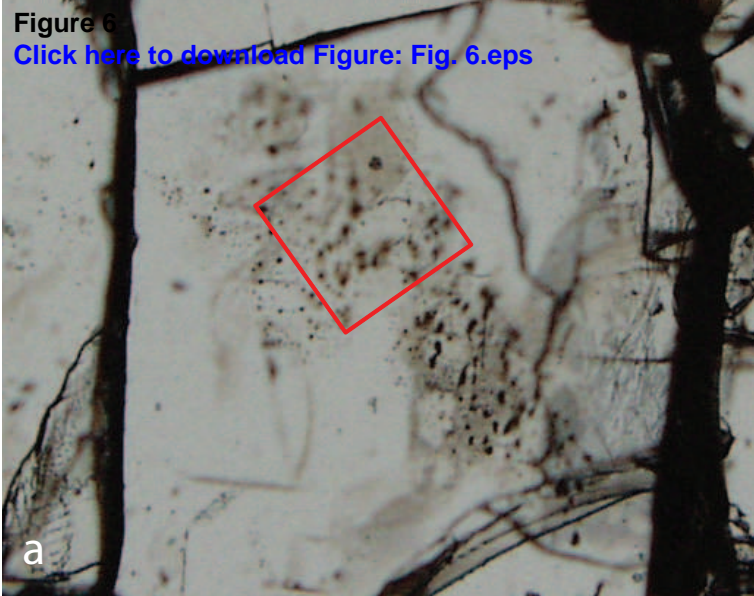


Figure 7
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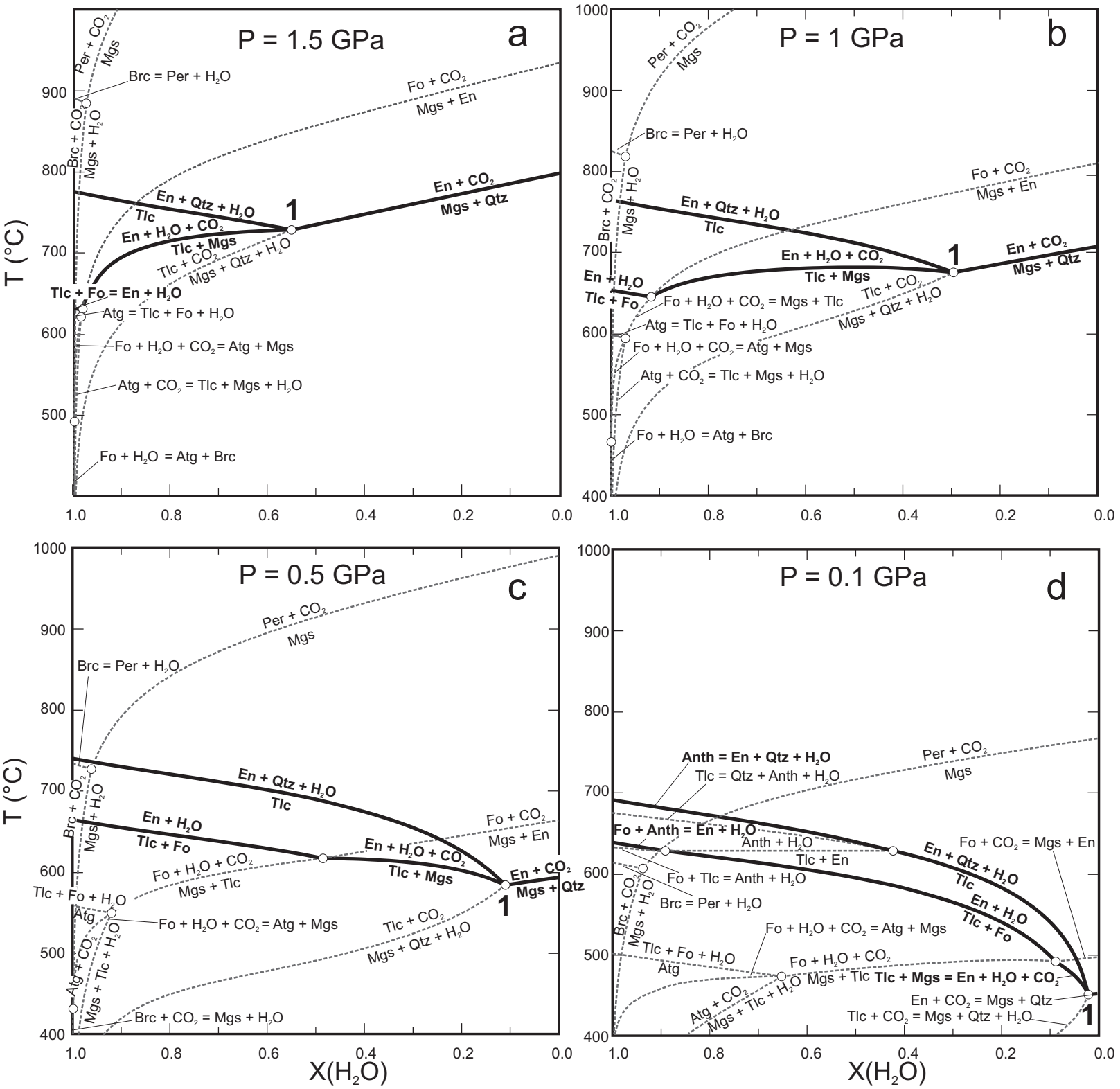


Table 1 - Sample description

Peridotites						CO ₂ -rich fluid inclusions						
Locality	Host rock	Rock type (n° of samples)	Texture	Mineralogy (vol%)	P-T conditions	Host	Tm _{CO2} (°C)	ThL _{CO2} (°C)	ThsL _{CO2} (°C)	TsL _{CO2} (°C)	Tm _{Clat} (°C)	P from isochores
Hawaii Oahu, Salt Lake Crater	Honolulu volcanics: Alkali basalt, Basanite, Nephelinite lavas	Grt Pyroxenite (4)	granular	Ol (5-15)	1000 °C	Ol	-56.8/-56.6	-56.6/25				>1.8 GPa
				Opx (5-10)	> 4.5 GPa	Opx	-56.8/-56.6	-56.6/24	-57.8/-56.6	-57/-56.5		>1.8 GPa
				Cpx (65-85) Grt-Spl (1-6) Phl (0-traces)		Cpx	-57/-56.6	-56.6/9.8	-58.2/-56.7	-57.9/-50.8		
Ethiopian volcanic plateau, Injibara	Basanite lavas	Spl Lherzolite (6)	protogranular to porphyroclastic	Ol (50-70)	950–1015 °C	Ol1	-57.6 / -56.5	-30.5 / 27.3			2.7	1.4–1.5 GPa
				Opx (20-30)	1.3–2 GPa	Opx1	-57.6 / -56.2	-39.2 / 30.9			5.6	
				Cpx (10-20)		Cpx	-57.9 / -56.3	-33.1 / 30.9				
				Spl (2-7) Prg (1)								
Italy Sardinia, Mt. Lisiri	Alkali basalt scoriae	Spl Pyroxenite (2)	granular	Ol (8-10)	950-1050 °C	Ol	-56.5	-13.8 / -4.8				0.95 GPa
				Opx (10-12)	0.9-1.5 GPa	Opx	-56.8 / -56.6	-24 / 9.3				
				Cpx (80-85) Spl (1-4) Phl (1-2)		Cpx	-56.7 / -56.5	-14 / 29.3				
		Spl Dunite (3)	porphyroclastic	Ol (90-95)		Opx1	-56.6	-11.7 / 3				1 GPa
				Opx (<1) Cpx (1-6) Spl (1-3)		Cpx	-57 / -56.6	-27.3 / 26.1				
Central Italy Torre Alfina	Lamproite lavas	Spl Harzburgite, Spl Dunite (3+1)	protogranular	Ol (80-95)	950-1080 °C	Opx1	-	-				1.2 GPa*
				Opx (3-12)	1.2-1.6 GPa							
				Cpx (1-4) Spl (1-4) Phl (1-10)								

Ol = Olivine; Opx = Orthopyroxene; Cpx = Clinopyroxene; Spl = Spinel; Grt = Garnet; Prg = Pargasite; Phl = Phlogopite; Tm = temperature of melting; ThL = temperature of homogenization to liquid; ThsL = temperature of homogenization to liquid in presence of solid CO₂ - superdense CO₂ inclusions; TsL = temperature of solid CO₂ final melting - superdense CO₂ inclusions; Hhl = hydrohalite; Clat = clathrate; Ol1, Opx1 = olivine and orthopyroxene porphyroclasts; * Pressures derived from Raman CO₂ density data (cf., Frezzotti et al., 2012).

Table 2 - Detection of water and solutes in fluid inclusions in mantle mineral using different analytical techniques

Mantle Rocks				Water and solutes in individual fluid inclusions					
Locality	Rock type	Hydrous Minerals	Host Mineral	Analytical technique					Fluid composition
				Microsc.	Microther.	Raman	FT-IR	EDS Microprobe	
Canary*	Sp Lherz.	No	Ol	No	No	Talc - Magnesite	-	Talc - NaCl	CO ₂ + H ₂ O, SiO ₂ and NaCl
	Sp Harz.		Opx	No	No	-	-	No	
			Cpx	No	No	-	-	No	
Hawaii	Grt Pyrox.	No	Ol	No	No	H ₂ O - CO ₂	-	No	CO ₂ (Carbonate melt) + H ₂ O, H ₂ S and N ₂
			Opx	No	No	H ₂ O - CO ₂	-	-	
			Cpx	No	No	H ₂ O - CO ₂	-	No	
			Grt	No	No	No	-	-	
Ethiopia	Sp Lherz.	Prg	Ol	No	No	Talc/Clinocllore (rare) Magnesite - H ₂ O - CO ₂	H ₂ O - OH ⁻	Magnesite - Talc	CO ₂ + H ₂ O, SiO ₂ , KCl and NaCl
			Opx	Yes	Yes	H ₂ O - CO ₂	H ₂ O	-	
			Cpx	No	No	-	No	-	
Sardinia	Sp Pyrox.	Phl	Ol	No	No	Talc - Magnesite	-	K, Cl, S, Ca, Na	CO ₂ + H ₂ O, SiO ₂ , KCl, NaCl, CaSO ₄
	Sp Dun.		Opx	No	No	Talc (rare) - Magnesite	-	K, Cl, S, Ca, Na	
			Cpx	No	No	Gypsum (rare) Dolomite - Talc (rare)	-	-	
Central Italy	Sp Harz.	Phl	Opx	No	No	H ₂ O - CO ₂ - S ₈	-	-	CO ₂ + H ₂ O and S
	Sp Dun.		Cpx	No	No	No	-	-	

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.