Fluid-related inclusions in Alpine high-pressure peridotite reveal trace element recycling during subduction-zone dehydration of serpentinized mantle (Cima di Gagnone, Swiss Alps)

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Abstract

Serpentinites release at sub-arc depths volatiles and several fluid-mobile trace elements found in arc magmas. Constraining element uptake in these rocks and defining the trace element composition of fluids released upon serpentinite dehydration can improve our understanding of mass transfer across subduction zones and to volcanic arcs. The eclogite-facies garnet metaperidotite and chlorite harzburgite bodies embedded in paragneiss of the subduction melange from Cima di Gagnone derive from serpentinized peridotite protoliths and are unique examples of ultramafic rocks that experienced subduction metasomatism and devolatilization. In these rocks, metamorphic olivine and garnet trap polyphase inclusions representing the fluid released during high-pressure breakdown of antigorite and chlorite.

26 Combining major element mapping and laser-ablation ICP-MS bulk inclusion analysis, we
27 characterize the mineral content of polyphase inclusions and quantify the fluid composition.
28 Silicates, Cl-bearing phases, sulphides, carbonates, and oxides document post-entrapment
29 mineral growth in the inclusions starting immediately after fluid entrapment.

30 Compositional data reveal the presence of two different fluid types. The first (type A)
31 records a fluid prominently enriched in fluid-mobile elements, with Cl, Cs, Pb, As, Sb
32 concentrations up to 10^3 PM (primitive mantle), $\sim 10^2$ PM Tl, Ba, while Rb, B, Sr, Li, U
33 concentrations are of the order of 10^1 PM, and alkalis are ~ 2 PM. The second fluid (type B)
34 has considerably lower fluid-mobile element enrichments, but its enrichment patterns are
35 comparable to type A fluid.

36 Our data reveal multistage fluid uptake in these peridotite bodies, including selective
37 element enrichment during seafloor alteration, followed by fluid-rock interaction along with
38 subduction metamorphism in the plate interface melange. Here, infiltration of sediment-
39 equilibrated fluid produced significant enrichment of the serpentinites in As, Sb, B, Pb, an
40 enriched trace element pattern that was then transferred to the fluid released at greater
41 depth upon serpentine dehydration (type A fluid). The type B fluid hosted by garnet may
42 record the composition of the chlorite breakdown fluid released at even greater depth.

43 The Gagnone study-case demonstrates that serpentinized peridotites acquire water and
44 fluid-mobile elements during ocean floor hydration and through exchange with sediment-
45 equilibrated fluids in the early subduction stages. Subsequent antigorite devolatilization at
46 subarc depths delivers aqueous fluids to the mantle wedge that can be prominently enriched
47 in sediment-derived components, potentially triggering arc magmatism without the need of
48 concomitant dehydration/melting of metasediments or altered oceanic crust.

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50

51 **1. Introduction**

52 Serpentinites affect major tectonic and geochemical processes on Earth. Because of their
53 abundance in oceanic lithosphere and in subduction zones, serpentinites affect the water
54 budget and the geochemical-geophysical properties of slabs and overlying mantle (Ulmer and
55 Trommsdorff, 1995; Cannat et al., 1995; Rüpke et al., 2004; Früh Green et al., 2004).
56 Increasing importance is now given to interface domains between subducting and overlying
57 plates, where serpentinite either forms kilometre-thick layers derived from hydration of
58 supra-subduction mantle (Bostock et al., 2002), or occurs in tectonic melanges atop the slab,
59 as matrix and as blocks of variable size and provenance (Bebout, 2007). In such
60 environments, the low-viscosity and high water content of serpentinite control deformation
61 focussing, fluid release and mass transfer (Gerya et al., 2002; Hyndman and Peacock, 2003;
62 Bebout, 2007). The role of serpentinite in element transfer from slabs to arc magmas is
63 debated. Sediments and altered oceanic crust are identified as the reservoirs delivering
64 incompatible elements to arcs (e.g. Plank and Langmuir, 1993; Elliott, 2003). It has been
65 proposed that element extraction from such rocks is boosted by fluids released by
66 serpentinite dehydration (Hermann et al., 2006; Kessel et al., 2005b; Spandler and Pirard,
67 2013). However, it is increasingly shown that serpentinites have the capacity to storing
68 volatiles and fluid-mobile elements sequestered during oceanic alteration, or during
69 interaction with slab-fluids circulating in subduction-zone environments (Hattori and Guillot,
70 2003; Scambelluri et al., 2004a; Sharp and Barnes, 2004; Savov et al., 2005; Deschamps et al.,
71 2011; 2013; Kendrick et al., 2011, 2013; John et al., 2011; Spandler et al., 2011; Alt et al., 2013;
72 Evans et al., 2014; Bebout, 2014). Once stored in serpentinite, these elements are
73 progressively released by the prograde dehydration reactions
74 chrysotile ± lizardite + SiO_{2,aq} = antigorite + fluid (1),
75 antigorite + brucite = olivine + fluid (2)

antigorite = olivine + orthopyroxene + fluid (3).
Reaction (1) takes place during early subduction (200-300 °C) beneath accretionary wedges and liberates trace-element charged fluids (Kodolanyi and Pettke, 2011). Reaction (2) occurred in eclogite-facies Alpine serpentinites, showing rock- and vein-forming antigorite+olivine-bearing parageneses. The fluid is Cl-rich and contains variable amounts of B and Li, besides other fluid-mobile elements (Scambelluri et al., 2004a; Scambelluri and Tonarini, 2012). Reaction (3), experimentally reproduced from ~60 km to subarc depths, releases 5-10wt% H₂O (Ulmer and Trommsdorff, 1995). Additional fluid is released by chlorite breakdown to garnet-bearing assemblages (Fumagalli and Poli, 2005; Dvir et al., 2011). Dvir et al. (2011) experimentally determined the major element composition of fluids in equilibrium with lherzolite across the chlorite-out reaction. No constraints from natural samples yet exist on the chlorite-dehydration fluids.

Serpentinite breakdown via reaction (3) is recorded at Cerro del Almirez (Spain), where chlorite harzburgite crops out as discrete rock unit, and at Cima di Gagnone (Central Alps), where metaperidotite blocks are embedded in a paragneiss sequence. At both localities the serpentinitized protoliths are preserved either as relict bodies with non-tectonised contacts to the chlorite harzburgite (Almirez; Trommsdorff et al., 1998), or as antigorite inclusions in peak eclogite-facies minerals (Gagnone; Scambelluri et al., 2014). Polyphase inclusions representative of the antigorite breakdown fluids from natural samples have been analysed so far only in the Almirez rocks. These inclusions are characterized by enrichments in B, Li, alkalis, Pb and Sr (Scambelluri et al., 2004a,b). Comparable fluid compositions were reproduced during experimental dehydration of natural Almirez serpentine (Spandler et al., 2014). These findings show that de-serpentinisation fluids are viable metasomatic agents for the subarc mantle.

100 Exchange with surrounding sedimentary rocks can cause serpentinite enrichment in
101 specific tracers like As, Be, Sb, B, radiogenic Sr, Pb and isotopically light B (Hattori and Guillot,
102 2007; Marchesi et al., 2013; Harvey et al., 2014; Scambelluri et al., 2014; Angiboust et al.,
103 2014; Lafay et al., 2013; Cannaò et al., 2015). Element addition to serpentinite may occur
104 during prograde burial (Deschamps et al., 2011; Scambelluri et al., 2014), or during fluid
105 channelling along shear zones in subducting slabs (Angiboust et al., 2014).

106 Although much work has been done to understand serpentinite behaviour in subduction
107 zones, direct analyses of de-serpentinisation fluids are still few (Scambelluri et al., 2001;
108 2004a, b; Tenthorey and Hermann, 2004; Spandler et al., 2014). Here we address this issue by
109 analysing fluid-related inclusions in eclogitic olivine and garnet from the Gagnone
110 metaperidotites. Because these rocks record influx of sediment-equilibrated fluid during
111 prograde subduction metamorphism (Scambelluri et al., 2014), they represent proxies of
112 mantle metaperidotite metasomatized by slab fluids, as occurs in melange (Bebout, 2007)
113 and/or in supra-subduction zone mantle (Hyndman and Peacock, 2003; Savov et al., 2005).
114 We present textural observations and inclusion analysis, aiming at quantifying the
115 composition of serpentine-breakdown fluids and constraining element recycling during
116 subduction.

117

118 **2. Geologic and petrologic background**

119 The Cima di Gagnone (Adula-Cima Lunga Unit, Central Alps) garnet metaperidotite and
120 chlorite harzburgite presented in this paper form lenses inside paragneiss (Fig. 1A). Other
121 peridotite bodies (Alpe Arami, Duria) occur in the Southern Adula unit. They are exposed
122 along a continuous horizon and, like Gagnone, they record eclogite-facies metamorphism and
123 are associated with pelitic, mafic and granitoid rocks of the European continental margin
124 involved in Alpine subduction (Evans and Trommsdorff, 1978; Pfiffner and Trommsdorff,

125 1998). In Adula, the eclogitic metamorphism pre-dates a collision-related amphibolite-facies
126 stage (Heinrich, 1982). The Adula rock association has been interpreted as a '*lithospheric*
127 *melange*' (Trommsdorff, 1990) formed in a *tectonic accretionary channel* representative of
128 plate-interface environments (Engi et al., 2001; Scambelluri et al., 2014).

129 Among the Gagnone metaperidotites, chlorite harzburgite lenses are the most
130 widespread; garnet metaperidotite is much less frequent (Fig. 1A). The chlorite harzburgite
131 bodies host basaltic eclogite and metarodingite. The latter rocks indicate that before
132 subduction the ultramafic host was exposed on the seafloor and serpentinized (Evans and
133 Trommsdorff, 1978). Petrography and pressure-temperature estimates of the Gagnone garnet
134 metaperidotite document a peak eclogite-facies paragenesis (olivine, clinopyroxene,
135 orthopyroxene, Mg-hornblende, garnet) crystallized at 800-850 °C and maximum 3 GPa (Fig.
136 1B; Evans and Trommsdorff, 1978; Pfiffner and Trommsdorff, 1998; Nimis and Trommsdorff,
137 2001; Scambelluri et al., 2014). In garnet metaperidotite, peak poikiloblastic garnet encloses
138 relict inclusions of prograde chlorite and Ca-amphibole (Scambelluri et al., 2014).
139 Thermodynamic modelling of the chlorite harzburgite suggests that the eclogite-facies
140 paragenesis (olivine, orthopyroxene, chlorite, F-Ti-clinohumite ± carbonate; Trommsdorff and
141 Evans, 1983; Scambelluri et al., 2014) crystallized between 650 °C (the antigorite-out
142 reaction) and 750-800 °C (the chlorite-out reaction); pressure likely was below 3GPa (Fig.
143 1C).

144 Metaperidotite compositions display decreasing Al₂O₃ and CaO with increasing MgO
145 concentrations and light-REE depletion. This compositional characteristic predates
146 subduction and was acquired during mantle melting and reactive melt flow in the oceanic
147 lithosphere (dataset and discussion in Scambelluri et al., 2014). The Gagnone metaperidotites
148 investigated here also record fluid-mobile element enrichment. Similarity in U, Pb, B, Li, and
149 Sr concentrations between the Gagnone metaperidotites and the present-day oceanic

serpentinites (Kodolanyi et al., 2012) suggests that these elements were acquired at least partially during initial serpentinisation by seawater-derived fluids (Scambelluri et al., 2014). Positive Be, As and Sb anomalies in the ultrabasic lenses (from several times to tens of times Primitive Mantle, PM, concentrations) suggest involvement of fluids equilibrated with metasediments during prograde subduction metamorphism (Fig. 1D). Equilibration of ultrabasic lenses with sediment-derived fluids is also suggested by their high contents of radiogenic Sr and Pb isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 0.71244 and 18.837, respectively; Cannaò et al., 2015), which approach the composition of associated paragneisses. Enrichments in the above fluid-mobile elements are common to all eclogitic minerals, indicating that open-system subduction metamorphism predated eclogite-facies dehydration of the ultrabasic lenses.

161

162 **3. Inclusion occurrence and petrography**

The inclusions hosted by the high-pressure metaperidotite minerals from Gagnone can be grouped as (1) monophase mineral inclusions and (2) polyphase inclusions, hosting several microcrysts intergrown in regular cavities.

The first group represents remnants of the pre-eclogitic mineral parageneses. In chlorite harzburgite, eclogitic fluorine-Ti-clinohumite hosts inclusions of prograde serpentine. In garnet metaperidotite, poikiloblastic garnet contains inclusions of prograde chlorite, amphibole, ortho and clinopyroxene. This indicates that these rocks, besides antigorite dehydration, also record later-stage chlorite breakdown and garnet formation (Fig. 1B; for detailed description and discussion see Scambelluri et al., 2014).

Reflected light microscopy has revealed several opaque phases, corresponding to light-grey chromite, magnetite and yellowish sulphides. The latter occur as inclusions in minerals, as rims on chromite, and as crystals interstitial to high-pressure minerals. Sulphides

175 frequently consist of intergrown crystals of variable chemical composition and are more
176 abundant in chlorite harzburgite.

177 Polyphase inclusions occur in garnet and olivine from garnet metaperidotite, and in
178 olivine from chlorite harzburgite.

179 *Garnet metaperidotite* contains 1-5 mm thick garnet layers and centimetre-sized garnet
180 crystals which may correspond to veins or fluid pockets (Figs. 2A,B). The coarse garnet
181 (sample MG160-C1) contains myriads of geometrically regular to irregular polyphase
182 inclusions. In general, they are randomly dispersed in garnet (Figs. 2C-F) and are interpreted
183 to represent primary fluid inclusions. Similar inclusions in garnet also occur along planes that
184 do not intersect the garnet grain-boundaries and corresponding to microcracks formed
185 during garnet growth (pseudosecondary inclusions, Fig. 2E). Comparably, the polyphase
186 inclusions in metamorphic olivine close to garnet (MG160-C1) are randomly distributed
187 inside olivine and also line along microcracks that do not cut the grain-boundaries, like
188 primary and pseudosecondary inclusions (Fig. 2E). The inclusions display opaque phases and
189 transparent, birefringent crystals. The polyphase inclusions exposed at the mineral surface
190 contain solids and yellowish sulphide microcrysts. Electron microscopy of olivine-hosted
191 inclusions revealed the presence of olivine reaction haloes between inclusion and the olivine
192 host, formed in response to fluid-olivine reaction still in the olivine stability field (Fig. 3A).
193 Olivine microcrysts were also identified inside the inclusions (Fig. 3B).

194 In *chlorite harzburgite*, the polyphase inclusions are hosted in metamorphic olivine from
195 coarse undeformed samples (MG304-92-1, MG304-92-2). In such samples, rock-forming
196 magnesite pertains to the high-pressure assemblage (Fig. 3C; MG304-92-2) and is partly
197 replaced by rims of retrograde dolomite. Chlorite harzburgite also shows sulphide inclusions
198 in minerals and sulphides interstitial to high-pressure minerals (Fig. 3D). As for the garnet
199 metaperidotite, the polyphase inclusions are regular to irregular in shape, are mostly

200 randomly dispersed in the host minerals, range in size from several micrometers (the
201 majority) to a few tens of micrometers, and contain opaque crystals together with
202 transparent, birefringent phases (Fig. 3E,F). Inclusions rarely follow pseudosecondary trails.
203 Scanning electron microscopy shows the occurrence of olivine (like in Fig. 3B) and of sulphide
204 microcrysts inside inclusions.

205

206 **4. Fluid inclusion data reduction**

207 Major element concentrations in inclusion-forming minerals, elemental maps of inclusions,
208 scanning electron microscopy of inclusions, and analysis of the trace element composition of
209 inclusions and hosts were performed by electron probe microanalysis (EPMA), scanning
210 electron microscopy and laser-ablation-ICP-MS at the Universities of Milano, Genova, and
211 Bern. Methods and operating conditions are described in the Analytical Methods repository
212 file.

213 During LA-ICP-MS analysis, individual polyphase inclusions fully enclosed in host
214 minerals are drilled out completely, to produce a signal consisting of pure mineral and mixed
215 inclusion+host (Fig. 4). This signal mixture of unknown proportions of host plus inclusion
216 material must be deconvolved to obtain a pure inclusion signal to be quantified following the
217 principles reported in Halter et al. (2002), Pettke (2006) and Pettke et al., 2012 (with
218 stringent limit of detection, LOD, calculation). Readers are referred to these papers for the
219 constraints required and the mathematical procedures employed. Here we display in
220 Repository Table R4 all inclusion analyses, discussing why some analyses are interpreted as
221 unreliable and discarded from the data set. The inclusions with consistent compositional
222 patterns used for interpretation are presented in Table 1. For reduction of garnet- and
223 olivine-hosted inclusions we adopted the approaches described below at points (1) and (2).

224 (1) Garnet-hosted fluid inclusions (sample MG160-C1).

225 To define the internal standard for such inclusions, we considered the compatible behaviour
226 of iron in the garnet-aqueous fluid system at 4 GPa/800 °C for basaltic bulk composition
227 ($KD_{\text{Fe}(\text{fluid-grt})}=0.017$; Kessel et al., 2005a). An average FeO concentration of 10.5wt% for the
228 host garnet (achieved from electron probe analyses) thus yields ~0.17wt% FeO in the fluid. In
229 absence of constraints on the oxidation state of Fe in the fluid, all iron was taken as FeO. We
230 further assumed a total dissolved load of 20wt% for the fluid inclusions, estimated on the
231 basis of fluid compositional data at 4 GPa/800 °C (Dvir et al., 2011; Kessel et al., 2005a). With
232 this approach for data reduction, 3 out of 6 high-quality inclusion analyses returned a
233 constant SiO₂ concentration of ~10wt% (Table 1). This SiO₂ concentration was then employed
234 to calculate the element concentrations of the other 3 inclusions, which returned a consistent
235 FeO concentration of ~2.1wt% instead of the inferred 0.17wt%. Interestingly, this FeO
236 concentration is much closer to that expected on the basis of $KD_{\text{Fe}(\text{fluid-grt})} = 0.15$ obtained by
237 Dvir et al., 2011, for an aqueous fluid-lherzolite composition at 5 GPa - 800 °C (note the much
238 higher pressure conditions compared to the Gagnone samples). These data suggest that fluid
239 trapped in garnet has variable FeO (Table 1).

240 (2) Olivine-hosted inclusions were analysed for the garnet metaperidotite MG160-C1 and the
241 chlorite harzburgite MG304-92-2.

242 (2a) For data reduction of olivine-hosted inclusions in the garnet metaperidotite, Na₂O was
243 employed as internal standard. Assuming low concentrations of ~0.1wt% Na₂O (as obtained
244 for the garnet-hosted inclusions) led to questionable results for analyses 21frc03, 04, 05, and
245 10 (Table R4). Analysis 21frc04 was discarded because it returned a Na₂O/TiO₂ ratio of 0.08
246 and elevated FeO, suggesting accidental entrapment of a Ti-mineral (ilmenite?). Inclusions
247 21frc03 and 21frc05 were also discarded because the estimated molar Na/Cl ratios of 0.9 and
248 1.3 (assuming Na₂O = 0.1wt % for data reduction), respectively, were clearly different from
249 the remaining inclusions (see below). Inclusion 21frc10 was also discarded because of its low

250 Na₂O and Cl concentrations that are inconsistent with the inclusions presented below. To
 251 calculate the concentrations of the remaining inclusions, model calculations were performed
 252 by incrementally increasing the assumed Na₂O concentrations of the inclusions. For Na₂O =
 253 0.5wt% results were obtained for 6 inclusion analyses (21frc06, 21frc08, 21frc09, 21frc11,
 254 21frc12, 21frc13; Table R4). Interestingly, 5 of these show consistent molar Na/Cl ratios of
 255 between 0.33 and 0.46. Inclusion 21frc06 gave a Na/Cl value of 0.64, suggesting partial Cl loss
 256 during analysis; this inclusion was therefore discarded. For the inclusions with uniform molar
 257 Na/Cl ratios, all but inclusion 21frc08 (FeO below its LOD, thus suggesting partial loss of
 258 inclusion content during analysis) returned a FeO concentration of between 1.0 and 1.6 wt%.
 259 We therefore consider the trace element compositions of inclusions 21frc09, 21frc11,
 260 21frc12, and 21frc13 reliable and worth further evaluation (Table 1).

261 (2b) For chlorite harzburgite MG304-92-2 (Table R4), we employed 0.01wt% Na₂O as the
 262 internal standard and 10wt% of total dissolved solids. These assumptions are based on the
 263 facts that (i) primary inclusions in olivine were likely entrapped at lower P-T than those in
 264 garnet (and thus the total dissolved solids are assumed to be lower based on the data of
 265 Kessel et al., 2005a,b; Dvir et al., 2011), and (ii) that the assumption of 0.5wt% Na₂O used for
 266 the olivine-hosted inclusions did not return inclusion concentration data. Model calculations
 267 were thus performed by incrementally decreasing Na₂O concentrations in the inclusions,
 268 obtaining a consistent data set for Na₂O=0.01wt%. With these constraints, inclusion
 269 concentrations could not be calculated for 6 out of 16 inclusions (the resulting total of major
 270 element oxides variably exceeded the 10wt% total), indicating that they represent mixtures of
 271 fluid inclusions and accidentally trapped Cr and Al-bearing Fe-rich spinel. Of the remaining
 272 inclusions, that returning an MgO concentration below its LOD (analysis 21fra04), the one
 273 with an MgO/SiO₂ abundance ratio of 3.1 (instead of 0.8 as obtained for the other inclusions)
 274 and those with an Al₂O₃ > 1.5wt% and Cr > 1400µg/g (analyses 21fra06, 21fra12 and 21fra17;

again indicative of minor accidentally entrapped Cr and Al-bearing Fe-rich spinel crystals) were discarded. Finally, 5 inclusion analyses remained with consistent inclusion element concentrations (Table 1).

Uncertainties on inclusion element concentrations obtained by these procedures are larger for elements enriched in the host mineral than for incompatible elements (Halter et al., 2002). Consequently, the PM-normalized trace element patterns presented here are insensitive to data reduction uncertainties for incompatible elements, while data for compatible elements must be considered semi-quantitative.

5. Mineral content and major element composition of inclusions

The elemental maps of inclusions and microprobe analysis of inclusion-forming minerals are shown in Figure 5, in repository Figure R1 and in Tables R1, R2, R3.

Garnet Metaperidotite. The maps of element distribution inside polyphase inclusions in garnet (Figs. 5, R1) reveal the presence of a Cl component. Chlorine is absent or below detection in the garnet host. Coincidence in the distribution of Cl, K and Fe suggests that inclusions contain chloride phases. Chlorine is not ubiquitous in garnet-hosted inclusions, because some of them do not reveal detectable amounts of this element (both by EPMA and LA-ICP-MS analysis). Figures 5 and R1 also show the presence of Cr-bearing oxides and of Cu- (and As) bearing sulphides, consistent with the LA-ICP-MS data. In all inclusions analysed, the remaining mineral phases correspond to Ca-amphibole, chlorite and spinel (Table R1). Such mineral infillings in garnet-hosted inclusions are confirmed by the high Ca and Cr concentrations shown by bulk inclusion analyses (Table 1). Electron microscopy suggests that some inclusion-filling mineral fractions derive from reaction with the host. Ca-amphibole + spinel intergrowths coating some polyphase inclusions in garnet may derive from fluid/host mineral reaction after inclusion entrapment. Alternatively, they may represent the preferred formation of fluid inclusions along with accidentally trapped spinel crystals. While the first

300 case poses no limitation to the bulk fluid composition, the second produces mixtures whose
301 composition is meaningless and therefore discarded from the dataset.

302 Comparable textures affect the olivine-hosted inclusions in garnet metaperidotite (Fig. 5).
303 Olivine from sample MG160-C1 contains inclusions with Cr-bearing magnetite, Cl-bearing
304 phase and Ni-sulphide, of which the magnetite (or ilmenite?) seems to be at least in part
305 trapped accidentally (see discussion of inclusion LA-ICP-MS data reduction above). The
306 sulphides here differ from sulphide in the garnet-hosted inclusions because they lack Cu, and
307 contain Ni as a major component (Table R3). As a whole, analyses of the olivine-hosted
308 inclusions yield much more Ni than the garnet-hosted inclusions. This, together with the
309 reaction haloes of Mg-silicates (olivine and/or serpentine) between inclusions and olivine
310 hosts (Fig. 3A), might be due to post-entrapment diffusional equilibration between fluid and
311 mineral host.

312 *Chlorite harzburgite*. Inclusions were investigated in carbonate-free (MG304-92-1) and
313 carbonate-bearing chlorite harzburgite (MG304-92-2), where magnesite and dolomite are
314 peak and retrograde rock-forming minerals, respectively. Inclusions in olivine of the
315 carbonate-free sample contain Fe-oxide, a Cl-bearing phase, and Ni-sulphide (Fig. R1). The
316 opaque minerals differ from those of inclusions in garnet for lower Cr content of the oxide and
317 for presence of Ni as main sulphide component (Table R3). As for the garnet-hosed inclusions,
318 the above opaque phases are associated with chlorite and serpentine.

319 In the carbonate-bearing sample MG304-92-2 magnesite occurs as a rock-forming
320 mineral coexisting with high-pressure olivine, orthopyroxene and chlorite (Fig. 3C) and is
321 overgrown by retrograde dolomite. In this rock, magnesite also occurs as an inclusion-
322 forming mineral together with serpentine, chlorite, and magnetite. This finding indicates the
323 presence of carbon species in the dehydration fluid of this sample. Interestingly, the inclusion
324 magnesite also shows partial replacement by dolomite. This feature, together with evidence of

inclusion-olivine replacement by serpentine (Fig. 3B), suggests post-entrapment precipitation of high-pressure phases within fluid-inclusions, followed by their replacement during back-reaction with the inclusion fluid during retrograde metamorphism.

6. Trace element composition of inclusions

LA-ICP-MS analyses of inclusions in the Gagnone metaperidotites are shown in Tables 1 and R4. The time-resolved analyses of inclusions in garnet (Fig. 4A) and olivine (Figs. 4B,C,D) reveal prominent signals for fluid-mobile elements and LILE. Figure 6 portrays the PM-normalized inclusion compositions (McDonough and Sun, 1995) together with previously published bulk-rock compositions (Scambelluri et al., 2014), showing a good fit with the inclusion data.

In garnet metaperidotite, the olivine-hosted inclusions display elevated concentrations of Cs, Rb, Ba, Pb, As, Sb, Sr and Cl (up to 1000 PM) and moderate enrichments of B, U and partly Li (concentrations up to 10 PM; Fig. 6A). Due to the smaller beam-size employed for inclusion analysis (LODs negatively correlate with beam-size) only a few trace elements returned significant concentrations for the host olivine. For this reason, the fluid/olivine distribution coefficients obtained from these analyses are restricted to a few elements. Moreover, because many elements in the host olivine were measured close to their respective LODs or are enriched in the host mineral, variance of the data is large. Hence, $KD_{\text{(fluid/olivine)}}$ for inclusion-host olivine pairs range considerably and only orders of magnitude can be estimated (Si, Mg, Fe $\sim 10^1$; As $\sim 10^2$; Na, Sr, Pb $\sim 10^3$); the best data are obtained $KD_{\text{Ti(fluide/olivine)}}=0.5$ and $KD_{\text{Li(fluide/olivine)}}=4$. An alternative approach is to estimate $KD_{\text{(fluid/olivine)}}$ values by combining the fluid data with large-beam (and thus low LOD) analyses of olivine from the same rock sample (published in Scambelluri et al., 2014). This approach returns $KD_{\text{(fluid/olivine)}}=4$ for Li (identical to that above), for B=3 (consistent with Scambelluri et al., 2004a; Tenthorey and Hermann,

2004), for As=350, for Sr=33000, and for Sb=1230. Even with large beam sizes, olivine analyses did not return significant concentrations for several elements. In such cases, minimum $KD_{(\text{fluid/olivine})}$ values can be estimated based on the lowest element-specific LOD values obtained (plotted in Fig. 6A with an arrow pointing downwards). This way we obtain Rb=3500, Cs=10000, Ba=25000, Y=80, La = 830, Ce=650, Nd=40, Dy=20, Pb=8300 and U=90. Comparable fluid patterns were achieved in the water-basalt system at 4-6 GPa (Kessel et al., 2005b).

The garnet-hosted inclusions of this sample are different (Fig. 6B). The LILE and fluid-mobile element enrichments are less pronounced than for the olivine-hosted inclusions. Cesium, Rb, B, As, Sb and Li show PM-normalized values above 1 while most other elements are below 1. Significant measurements for elements in garnet were only obtained for MREE to HREE, Li, and Nb. The few, directly determined element distribution coefficients show $KD_{(\text{fluid/garnet})}$ values between ~ 0.2 and 0.05 for the REE (decreasing with increasing atomic number), and of the order of 10 for Li. $KD_{(\text{fluid/garnet})}$ values for Sr and Nb are around 4 and 1.7, respectively. Reporting minimum $KD_{(\text{fluid/garnet})}$ values for the other elements (like for the olivine-hosted inclusions reported above) is not useful because the LODs for these elements are at the lower end of the ranges covered by element concentrations in the fluid (compare with Table R4).

The olivine-hosted inclusions in chlorite harzburgite (MG204-92-2) are different from the olivine-hosted inclusions in garnet metaperidotite MG160-C1 and resemble those hosted by garnet in this sample (Fig. 6C; Table 1). Concentrations relative to PM are again most enriched for As and Sb, followed by Cs and B. Lead shows 1PM concentrations, and the other elements are variably below PM values. Only a few of the host olivine element concentrations are significant; most elements were below the respective LODs. Estimated $KD_{(\text{fluid/olivine})}$ for As is about 100, while for B, Nb, Ta, Zr it is around 1 and for Li it is ~ 0.2 .

375 Altogether, prominent enrichments in As and Sb and variably enriched large ion lithophile
376 elements plus positive PM-normalized anomalies for B and, to a lesser extent, Pb characterize
377 all inclusion compositions, while Sr is only enriched in the olivine-hosted inclusions of garnet
378 peridotite (MG160-C1). These olivine-hosted inclusions contain a prominent halogenide
379 component (~1.5wt% Cl) that is absent from inclusions hosted by garnet or by olivine from
380 chlorite harzburgite (Table 1), thus demonstrating that two different fluid inclusion types are
381 present in these samples. The lowest relative LILE enrichment is revealed by olivine-hosted
382 inclusions of chlorite harzburgite MG304-92-2, consistent with the corresponding low bulk-
383 rock values of 0.014µg/g Cs, 0.052µg/g Rb, 0.83µg/g Ba and the depleted LREE
384 concentrations (e.g., 0.085µg/g La) indicative of prominent melt depletion prior to hydration.

385

386 **7. Discussion**

387 The garnet metaperidotite and chlorite harzburgite from Cima di Gagnone are the high-
388 pressure breakdown products of mantle rocks affected by multiple stages of oceanic- and
389 subduction-related serpentinisation and element influx (Evans and Trommsdorff, 1978;
390 Scambelluri et al., 2014). Positive anomalies in As, Sb, Be, B, elevated contents in radiogenic Sr
391 and Pb, low $\delta^{11}\text{B}$ characterizing bulk rocks and high-pressure minerals, point to element
392 transfer from paragneiss to the serpentinized peridotite protoliths during subduction burial
393 (Scambelluri et al., 2014; Cannaò et al., 2015). These geochemical characteristics identify
394 Gagnone as a prime example of mantle rocks recording fluid-mediated element exchange with
395 metasediments in plate-interface subduction melanges. The Gagnone metaperidotites may
396 also offer a proxy for the geochemical characteristics of the supra-subduction zone mantle
397 altered by sediment-equilibrated slab fluids. Such element exchange is followed by the high-
398 pressure dehydration evolution shown in Figure 1B,C. Based on petrography (relict
399 serpentine and chlorite + amphibole inclusions in eclogite-facies minerals) and on phase

relations, chlorite harzburgite and garnet metaperidotite underwent antigorite breakdown. In garnet peridotite this event was followed by chlorite dehydration.

7.1. *Post-entrapment modifications of inclusions*

The garnet- and olivine-hosted polyphase inclusions presented here further constrain the process of metaperidotite dehydration. In terms of texture, the inclusions are randomly distributed in high-pressure olivine and garnet, or are bound to microcracks that do not intersect grain boundaries (Fig. 2E). They thus correspond to primary and pseudosecondary fluid inclusions trapped during growth of the above eclogite-facies minerals. Despite deriving from water-rich fluids, the Gagnone inclusions do not display an aqueous liquid phase today, but are filled with minerals. This indicates post-entrapment modifications that need to be addressed first.

Post-entrapment changes can be isochemical and non-isochemical: the latter need to be recognized in order to understand the significance of data. Post-entrapment crystallization in response to H or water loss does not pose analytical problems as long as the complete inclusion content is analysed, for example drilling-out entire inclusions from host minerals by LA-ICP-MS. Laboratory reheating and re-homogenization of inclusion contents is not viable because of H or water loss. Strictly, loss of H₂O solvent from inclusions qualifies the process of post-entrapment crystallization as non-isochemical; however, the total dissolved solid load may remain unchanged. Non-isochemical post-entrapment modifications include diffusive equilibration with the host mineral or possibly with the surrounding rock materials. In the case of Gagnone, this is indicated by magnetite crystallization in the inclusions. The model reaction fayalite (in olivine)+H₂O → SiO_{2(aq)} + magnetite + H⁺, followed by H-loss, documents gain of Fe and increased f_{O2} in the fluid inclusion upon crystallisation.

Evidence that mineral precipitation in inclusions began under high pressure-temperature

425 conditions is provided by crystallization of olivine onto the inclusion walls, by olivine micro-
426 crystals in inclusions (Fig. 3A,B), and by the presence of magnesite in inclusions from
427 magnesite-bearing chlorite harzburgite. Amphibole, spinel, chlorite and Cu-bearing sulphide
428 occur in garnet-hosted inclusions, while the olivine-hosted inclusions of the same sample and
429 of MG304-92-2 contain Mg-silicates and Fe-Ni sulphides without significant Cu (Figs. 5; R1).
430 These Ni-bearing sulphides may be a reaction product with the olivine host. The difference in
431 inclusion mineralogy may therefore indicate post-entrapment interaction between inclusions
432 and their host that certainly affected major element fluid inclusion composition. However,
433 incompatible trace element patterns likely remain unaffected, similar to what suggested for
434 high-pressure polyphase inclusions (e.g. Scambelluri et al., 2004a; Malaspina et al., 2006).
435 Therefore, the Gagnone polyphase inclusions can preserve relevant information on the
436 composition of high-pressure fluids and on major fluid-processes during the subduction cycle.

437 The similarity with polyphase inclusions from the Almirez chlorite harzburgite is striking.
438 Both inclusion types contain today chlorite, olivine (or serpentine), opaque minerals plus
439 additional minor phases (chlorides in Gagnone, apatite in Almirez; Scambelluri et al., 2001).
440 Scambelluri et al. (2001; 2004a) estimate that the water-rich antigorite breakdown Almirez
441 fluid inclusions (with salinity between 0.4 and 2wt% NaCl) were desiccated by precipitation
442 of hydrous silicates and H⁺ loss during post-entrapment fluid inclusion modification.

443

444 *7.2 Fluid inclusion compositions*

445 Concerning the fluid components, the elemental maps (Figs. 5, R1) and the sulphide analysis
446 (Fig. 7) complement the inclusion data and help identifying the elements transported by the
447 fluid. Elemental mapping locally revealed the presence of Cl, often along with K and Fe.
448 Chlorine anomalies only pertain to polyphase inclusions and are absent in other rock
449 domains. For this reason we propose that Cl was a high-pressure fluid component, as pointed

450 out by the significant Cl concentrations measured in olivine-hosted inclusions from garnet
451 peridotite MG160-C1 (Table 1). Serpentinite dehydration is known to release chlorine-
452 bearing fluids, especially during the chrysotile and the antigorite+brucite breakdown
453 reactions (1) and (2) (Scambelluri et al., 1997; Kodolanyi and Pettke, 2011). Scambelluri et al.
454 (2004) estimated a bulk loss of 2wt% H₂O during this reaction. Chlorine concentrations in
455 antigorite dehydration fluids produced by reaction (3) are lower (0.4-2wt% NaCl in fluid;
456 Scambelluri et al., 2004a) because the larger amount of water produced by the antigorite
457 breakdown reaction (5-10wt% H₂O) strongly dilutes the fluid. Presence of chlorine in the
458 Gagnone polyphase inclusions therefore confirms that serpentinite dehydration releases Cl to
459 fluids.

460 The analysis of sulphide in different textural sites of garnet peridotite and chlorite
461 harzburgite points to a change in sulphide composition during rock evolution, probably
462 depending on fluid composition. Figure 7 shows variation in sulphide composition from
463 higher S and Fe concentrations in rock-forming grains (mineral inclusions and interstitial
464 minerals), to lower Fe and S and higher Ni and/or Cu in sulphide crystals inside inclusions. In
465 the Gagnone metaperidotites, formation of sulphide phases that are not stable in pristine
466 mantle rocks and in altered seafloor mantle indicates sulphur mobility during subduction
467 metamorphism and suggests presence of reduced sulphur in the high-pressure fluids.

468 The presence of magnesite in inclusions from chlorite harzburgite provides compelling
469 evidence that, besides water, carbon was also mobilized in the metaperidotite dehydration
470 fluid. The available data, however, do not constrain the C:O:H abundance ratios of the fluid at
471 entrapment conditions.

472

473 *7.2.1. Trace element inclusion compositions*

474 The trace element patterns of fluid inclusions presented here (Table 1) suggest the presence

475 of two types of fluids in these rocks. Type A, trapped in high-pressure metamorphic olivine of
476 garnet peridotite MG160-C1, is prominently enriched in fluid-mobile elements relative to PM
477 (concentrations up to 10^3 PM Cl, Cs, Pb, As, Sb; $\sim 10^2$ PM Tl; $\sim 10^1$ PM Rb, Ba, B, Sr; ~ 2 PM Na,
478 K). Type B is much less enriched in fluid-mobile elements and occurs both in garnet of sample
479 MG160-C1 (Figs. 4A; 6B), and in olivine of the chlorite harzburgite (Figs. 4B; 6C). However,
480 the PM-normalized patterns of the fluid types A and B are similar (Fig. 8A).

481 The combined enrichment in LILE and chalcophile elements coincides with what is
482 expected to be characteristic for a sediment-equilibrated fluid. Type A fluid thus records a
483 much more prominent sediment signal than does type B, a difference that can be related to
484 multiple dehydration stages of rocks recording different extents of pre-eclogitic interaction
485 with sediment-equilibrated fluids. In garnet peridotite, fluids A and B can be related to
486 different fluid-forming dehydration reactions and stages. For garnet peridotite MG160, fluid A
487 likely represents that released upon antigorite breakdown, while Fluid B (trapped in garnet
488 from this sample) represents that released at higher temperature during chlorite breakdown
489 (Fig. 1B). This sample thus records successive fluid release from an original serpentinite
490 heavily enriched in incompatible elements acquired during multiple hydration events on the
491 seafloor and during prograde subduction metamorphism. Although the fluid inclusions hosted
492 by olivine of the chlorite harzburgite MG304-92 most likely also represent the antigorite
493 dehydration product, their compositions are much lower in fluid mobile elements than fluid
494 type A and more closely resemble that hosted in garnet of the garnet lherzolite (Figs. 6, 8A).
495 We interpret this prominent difference to reflect the much more modest overall element
496 enrichment in the chlorite harzburgite as already revealed by bulk rock compositional data
497 (Scambelluri et al., 2014).

498 In summary, our analytical survey indicates that the chlorite harzburgite and the garnet
499 peridotite lenses from Gagnone trap fluids related to multiple hydration and dehydration

500 stages recorded by rocks affected by different degrees of interaction with sediment-derived
501 fluid prior to eclogitization.

502

503 *7.3. Relevance for trace element cycling along the subduction interface*

504 Presence of the same set of elements in the fluid-related inclusions and in the high-
505 pressure minerals grown during metaperidotite dehydration implies a recycling process. This
506 highlights the Gagnone metaperidotites as useful materials for understanding the composition
507 of subduction fluids released by such a metasomatized mantle reservoir, and for tracing fluid-
508 mediated trace element crust-mantle exchange. The P-T conditions of metaperidotite
509 recrystallisation (800-850 °C; 3 GPa) fit recent modelling of slab top temperatures in sub-arc
510 subduction domains (Syracuse et al., 2010), suggesting that the inclusions presented here are
511 representative of fluids released in such environments.

512 The Gagnone type A inclusions (related to antigorite-breakdown) are compared in
513 Figure 8B with inclusions in chlorite harzburgite from Cerro del Almirez (Scambelluri et al.,
514 2004b). At both localities the inclusions display comparable PM-normalized trace element
515 patterns, showing positive anomalies in fluid-mobile elements (Fig. 8B). This comparison
516 emphasizes that the de-serpentinisation fluids in the two localities display common features,
517 represented by Cs, B, Pb and Li concentrations exceeding those of PM. Input from sedimentary
518 reservoirs into serpentinites has been recently advocated for Almirez based on trace element
519 and Sr isotopic studies (Marchesi et al., 2013; Harvey et al., 2014). This might explain the
520 enrichment in crust-derived elements unusual in serpentinites formed by single-stage ocean
521 floor hydration, and increasingly found in ultramafic rocks evolved through subduction-zone
522 processes.

523 The PM-normalized pattern of the Gagnone type A inclusions also compares well with
524 compositions of the antigorite breakdown fluid reproduced during experimental dehydration

525 of natural serpentinite from Almirez (Fig. 8C) by Spandler et al. (2014). Figures 8B and D
 526 compare the antigorite-breakdown fluids presented here with the compositions of arc lavas
 527 from several locations (Kelemen et al., 2014). Where possible, the arc-lava dataset has been
 528 complemented with B, As and Sb contents (Bailey et al., 1989; Morris et al., 1990; Noll et al.,
 529 1996; Ryan et al., 1995; Ishikawa and Tera, 1997; Ishikawa et al., 2001; Leeman et al., 2004;
 530 Timm et al., 2012; Savov et al., 2006; Tonarini et al., 2011). Figures 8B and D show a fairly
 531 good overlap of fluids and arc lavas for Cs, Rb, Ba, B, Pb, As, Sb, Li, whereas other elements (e.g
 532 LREE, Na, Sr) deviate significantly. The correspondence between the Gagnone inclusions and
 533 arc lavas for the above elements helps to visualize the subduction component released to arcs
 534 by dehydrating serpentinite. Figure 8D illustrates the difference between the olivine-hosted
 535 inclusions in garnet peridotite, whose protolith shows larger extent of contamination by
 536 sediment-equilibrated fluid, and in chlorite harzburgite, derived from protoliths less affected
 537 by sediment-derived components. Figure 8D indicates that fluids released by serpentinites
 538 affected a larger extent of interaction with sediment-equilibrated fluids have higher budgets
 539 of LILE, chalcophile elements, Li and B. This comparison reveals the variability in serpentinite
 540 dehydration fluid composition and may offer an explanation for some of the prominent
 541 compositional variations reported for arc lavas.

542 In order to more generally address fluid-mediated element transfer, mineral/fluid
 543 partition coefficients (Fig. 8E) are derived from our data, using average compositional data of
 544 polyphase inclusions (Table 1) and of mineral hosts (see section 6). As expected, garnet has
 545 affinity for Zr, Y, HREE whereas olivine retains significant Li and B, as shown by $KD_{\text{(fluid/olivine)}}$
 546 close to 3 and 4, as also documented in previous studies (Tenthorey and Hermann, 2004;
 547 Scambelluri et al., 2004a). The mineral/fluid partition coefficients (Fig. 8E), together with the
 548 modal amounts of rock-forming olivine and garnet in the Gagnone garnet metaperidotite have
 549 been employed to reconstruct the composition of the serpentinite prior to antigorite

breakdown. Figure 8F shows that the trace element pattern of the model garnet metaperidotite protolith is comparable with serpentinites from various settings (Deschamps et al., 2013), the main difference being much higher absolute concentrations of fluid-mobile elements in the model Gagnone metaperidotite protolith. This prominent enrichment in LILE and chalcophile elements again emphasizes the sedimentary input recorded by the Gagnone garnet metaperidotite protolith. Therefore, they may represent an ultramafic end-member for uptake of crust-derived elements.

The capacity of serpentinized mantle to incorporate fluid-mobile elements was emphasized by Hattori and Guillot (2003) and by Deschamps et al. (2011), showing that As, Sb, B lost from dehydrating slabs at relatively low-temperature are transferred to altered ultramafic (mantle) lithologies. The high concentration of such fluid-mobile elements measured in the Gagnone bulk rocks, in the fluid-related inclusions and in the high-pressure minerals fits the above interpretation. Our trace element data (together with radiogenic Pb and Sr; Cannaò et al., 2015) thus offer a record of *‘fluid-transported’* elements from the country parashist into the melanged ultramafic bodies, elements that may be delivered later to subarc fluids.

The local-scale trace element transfer documented here for Gagnone may have larger-scale implications when considering mass transfer from slabs to supra-subduction zone mantle. Figure 9 shows two possible scenarios where serpentinite affected by sediment-derived fluids may impact on subduction-zone element recycling. In a first case (Fig. 9A), serpentinized mantle rocks (slab and/or mantle-wedge provenance) in a subduction-melange release antigorite- and chlorite breakdown fluids to the overlying mantle. If one extrapolates from the context of top-slab melange environment, and considers the pre-dehydration Gagnone serpentinite compositions (Fig. 8F) as representative of altered supra-subduction mantle wedge (Fig. 9B), the potential of ultramafic rock systems in storing and transporting

575 slab-derived elements from shallow (forearc) to deep subduction settings becomes
576 compellingly apparent. In Figure 9B, sediment-derived slab fluids infiltrate a layer of supra-
577 subduction mantle (dotted layer above the plate interface) that acquires Gagnone-like
578 compositions. As in Figure 9A, this layer recycles the antigorite and chlorite-breakdown fluids
579 to the mantle in a sequence of dehydration events. As stated previously (Hyndman and
580 Peacock, 2003; Savov et al., 2005; Hattori and Guillot, 2003; Scambelluri and Tonarini, 2012)
581 water and fluid-mobile element transfer from slabs to the forearc mantle can be followed by
582 downdrag of this altered mantle to subarc depths. Gagnone may therefore represent a highly
583 enriched end-member of this process.

584

585 **8. Conclusions**

586 The Gagnone chlorite harzburgite and garnet metaperidotite derive from serpentized
587 mantle protoliths recording two stages of element uptake: (i) hydration in ocean-floor
588 environments followed by (ii) exchange with sediment-derived fluids during burial in a plate-
589 interface melange environment. These events predated (iii) eclogite-facies dehydration at
590 sub-arc conditions (Scambelluri et al., 2014). Chlorite harzburgite essentially records high-
591 pressure breakdown of serpentine, whereas the garnet metaperidotite records a first event of
592 de-serpentinisation followed by chlorite breakdown to garnet.

593 The eclogite-facies olivine and garnet trap primary inclusions representing the fluid
594 evolved during breakdown of antigorite and chlorite, respectively. The inclusions display
595 fluid-mobile element enrichments (high Cl, S; variable Cs, Rb, Ba, B, Pb, As, Sb). Presence of
596 magnesite in inclusions inside the samples showing rock-forming magnesite indicates carbon
597 release to the aqueous fluid via decarbonation and/or carbonate dissolution.

598 The olivine-hosted inclusions in the garnet metaperidotite represent a fluid related to
599 antigorite breakdown (fluid A). It has the highest fluid-mobile element and LREE contents,

600 reflecting a sedimentary signal and the recycling of sedimentary components into the de-
601 serpentisation fluid. Lower degrees of enrichments of these elements in olivine-hosted
602 inclusions from chlorite harzburgite point to variable degrees of pre-eclogitic
603 alteration/enrichment of the Gagnone rocks.

604 The inclusions trapped in garnet (fluid B, representing the chlorite dehydration product)
605 display much lower fluid-mobile element concentrations, suggesting squeezing of a rock that
606 already delivered such components during antigorite breakdown.

607 Our observations indicate that the metaperidotite lenses in the Gagnone melange derive
608 from mantle rocks that sequestered fluid-mobile elements sourced from the surrounding
609 metasediments. Dehydration of such a metasomatized mantle provides trace element-
610 enriched fluids conveying inherited sedimentary components into the mantle wedge. We
611 confirm the tendency of serpentinized mantle to capture fluid-mobile elements and propose
612 that through fluid-mediated transfer from sediments during subduction-zone processing, the
613 serpentinised mantle can transfer of Cl, S, Cs, Rb, Ba, B, Pb, As, Sb to arc magmas.

614 The geochemical processes envisaged here for metaperidotites in a melange can apply to
615 the supra-subduction mantle altered by slab fluids. The shallow element release from slabs to
616 mantle, downdrag of this altered mantle and its subsequent (subarc) dehydration can transfer
617 crust-derived fluid-mobile matter to the mantle wedge (Hyndman and Peacock, 2003; Ruepke
618 et al., 2004; Savov et al., 2004; Scambelluri and Tonarini, 2012) without the need of
619 concomitant subarc dehydration/melting of metasedimentary slab components. Therefore,
620 the slab signature detected in arc lavas can result from geochemical mixing of sediment,
621 oceanic crust and ultramafic rocks, rather than being attributed to multiple fluids. In this
622 frame, the Gagnone inclusions represent a composite serpentinite-sediment fluid delivered to
623 the mantle wedge by serpentinite affected by subduction-zone processing.

624

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847 **Figure Captions**

848

849 Figure 1. A: Geological map of the Cima di Gagnone area, showing the outcrops of chlorite
850 harzburgite and garnet metaperidotite sampled. After Scambelluri et al. (2014), redrawn
851 after Pfiffner and Trommsdorff (1998) and Pfiffner (1999). Pressure-temperature
852 pseudosections for the Gagnone garnet peridotite (B) and chlorite harzburgite (C) (after
853 Scambelluri et al., 2014). Arrows show possible prograde paths joining early stage
854 assemblages, defined by monophase inclusions in high-pressure minerals, with the stability
855 fields achieved for peak eclogite-facies parageneses. Garnet peridotite in (A) records
856 antigorite and chlorite breakdown. C: Sb-As diagram showing the array of high-pressure
857 minerals and bulk rocks from Gagnone, comprised between Primary Mantle reservoirs and
858 pelagic clays (after Scambelluri et al., 2014).

859

860 Figure 2. Textures of garnet peridotite (A and B) and of polyphase inclusions in garnet (C to F)
861 (sample MG160-C1). Rocks contain garnet megacrysts likely representing fluid pockets in
862 garnet peridotite. F: close up of polyphase inclusions in garnet.

863

864 Figure 3. (A) and (B): scanning electron microscope images of olivine-hosted inclusions from
865 garnet peridotite and chlorite harzburgite, respectively. (A): olivine (ol) reaction halo
866 between the inclusion (inc) and the olivine host. (B): olivine microcrystal inside the inclusion
867 being replaced by serpentine. (C) Chlorite harzburgite showing an olivine + orthopyroxene
868 (opx) + chlorite + magnesite (mag) paragenesis. (D) Interstitial sulphide (lower left side of the
869 picture) in between high-pressure minerals and coarse sulphide inclusion in chlorite
870 harzburgite minerals. (E) Primary polyphase inclusions in high-pressure olivine from chlorite
871 harzburgite. (D) close up of polyphase inclusions in olivine.

872

873 Figure 4. Time-resolved fluid inclusion analyses. (A) is hosted by garnet, sample MG160-C1,
874 (B) is hosted by olivine, sample MG304-92-2, and (C,D) shows different elements of the same
875 inclusion hosted in olivine, sample MG160-C1.

876

877 Figure 5. Elemental maps, showing element distribution inside polyphase inclusions hosted in
878 olivine and in garnet from the garnet peridotite sample MG 160C1. Despite having the same
879 label, inclusion are from two different sites and hosts of this sample.

880

881 Figure 6. PM-normalized trace element compositions of polyphase inclusions and of their host
882 minerals. (A) shows the inclusions in olivine and (B) shows the inclusions in garnet from the
883 garnet peridotite MG160-C1. (C) portrays the inclusions in olivine from chlorite harzburgite
884 samples. Downward pointing arrows in (A) identify the respective limits of detections for host
885 olivine analyses. See text for implications regarding the two fluid types A and B from the
886 garnet metaperidotite and the chlorite harzburgite. The light grey background patterns report
887 the bulk-rock trace element compositions (after Scambelluri et al., 2014).

888

889 Figure 7. Plots of Ni+Cu and S vs. Fe of rock- and of inclusion-forming sulphides.

890

891 Figure 8. A: PM-normalized compositions of all analysed inclusions. B: trace element patterns
892 of antigorite-breakdown-related inclusions (from both garnet peridotite and chlorite
893 harzburgite) from Gagnone (grey area) and of average Almirez inclusions (black solid line;
894 data from Scambelluri et al., 2004b). Only reported are the elements common to the two
895 sample sets; As and Sb data are not available for Almirez. The light grey data points refer to
896 arc lavas from Kermadec (diamonds), Marianas (squares), Scotia (triangles), Aleutian (cross
897 with six arms); Cascades (dots) Costa Rica (crosses); Kamchatka (x symbol). (Data from Bailey

898 et al., 1989; Morris et al., 1990; Noll et al., 1996; Ryan et al., 1995; Ishikawa and Tera, 1997;
 899 Ishikawa et al., 2001; Leeman et al., 2004; Timm et al., 2012; Savov et al., 2006; Tonarini et al.,
 900 2011). C: trace element patterns of antigorite-breakdown inclusions Gagnone compared to
 901 the experimental antigorite-breakdown fluid inclusions in the P-T range of 3.5-4 GPa and 700-
 902 900 °C (Spandler et al., 2014). (D) The trace element data of the Gagnone antigorite-
 903 breakdown inclusions in olivine from the garnet peridotite (grey dots) and from chlorite
 904 harzburgite (white squares) are compared with the arc lava dataset (grey field and grey
 905 symbols in the background). Data source for the arc lava compositions is the same as in Figure
 906 B. (E) Mineral/fluid trace element partition coefficients (measured for fluid - host mineral
 907 pairs in black and minimum KD estimated from fluid inclusion data combined with mineral
 908 analyses from the same rock in grey symbols) for garnet peridotite. F: PM-normalized
 909 composition of the modelled Gagnone garnet peridotite prior to eclogite facies antigorite
 910 dehydration. The reconstructed composition only accounts for garnet and olivine, being the
 911 only phases for which fluid-mineral host partition coefficients are available. Amphibole, ortho
 912 and clinopyroxene have been omitted from this estimate due to lack of coupled
 913 measurements of fluid inclusion and host.

914

915 Figure 9. Possible geodynamic scenarios and implications for stepwise fluid loss from the
 916 Gagnone metaperidotites. The upper sketch shows a subduction system where the mantle
 917 wedge, the serpentized supra-subduction mantle, the plate interface and the downgoing
 918 slab are distinguished with different grey-scales. The white dashed lines correspond to the
 919 reaction isograds showing breakdown of antigorite (atg) and chlorite (chl) in hydrated
 920 ultramafic rocks. Figures A and B are larger-scale pictures of the domain within the rectangle
 921 shown in the upper sketch. Figure A shows a plate-interface subduction melange with a
 922 sediment-dominated matrix like Gagnone. Before crossing the antigorite breakdown reaction,

923 slab and wedge ultramafic rocks and the melange blocks correspond to antigorite + chlorite-
924 bearing peridotites. During antigorite breakdown these rocks dehydrate to chlorite-bearing
925 peridotites and release a prominent fluid pulse, followed by a later fluid pulse from chlorite-
926 breakdown, forming garnet peridotites. The different grey scales in the legend boxes indicate
927 the possible provenance of the melange blocks: light grey from slab and dark grey from mantle
928 wedge. In Figure B uprising slab fluids equilibrated with sediments produce a layer of
929 hydrated mantle wedge peridotite showing a Gagnone-like geochemical signature (e.g. Figure
930 8F). All figures are not to scale.

Figureg

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Garnet peridotite Mg160 C1

inclusions in garnet

inclusion in olivine

Figure 6

Figure 7

Figure 8

Figure 9

Table

Table 1

Table 1: LA-ICP-MS element concentration data for polyphase inclusions in garnet and olivine from Cima di Gagnone

		MG 160 C1; garnet host						MG 160 C1; olivine host				MG 304 92-2; olivine host				
Sample number		21frb04	21frb08	21frb09	21frb05	21frb06	21frb10	21frc09	21frc11	21frc12	21frc13	21fra03	21fra11	21fra14	21fra15	21fra18
Inclusion size (µm)		40	40	55	40	55	58	40	22	22	18	22	60	25	25	26
Mass																
SiO2	29	10.00	10.00	9.00	10.00	10.97	9.03	5.93	5.75	2.99	4.48	4.82	4.60	4.41	5.40	4.89
TiO2	49	0.0088	0.0041	0.0104	0.0105	0.0081	0.0129	0.0124	0.0073	0.0013	0.0313	<0.0002	0.0017	0.0127	0.0089	0.0008
Al2O3	27	3.68	2.24	4.63	3.06	2.84	4.68	0.0033	<0.0006	0.0009	0.0010	####	0.0025	0.0198	0.0012	0.0003
FeO	57	2.04	2.13	2.02	0.17	0.17	0.17	1.53	1.57	1.39	1.02	1.25	1.36	1.46	1.39	1.16
MgO	25	3.39	6.42	3.22	5.83	5.02	4.77	1.05	1.56	4.35	3.31	3.92	4.01	4.08	3.12	3.92
CaO	43	0.86	<0.01	1.10	0.74	0.80	1.24	0.91	0.56	0.72	0.62	<0.02	<0.008	<0.01	0.04	<0.03
Na2O	21	0.03	0.02	0.02	0.17	0.19	0.09	0.50	0.50	0.50	0.50	0.01	0.01	0.01	0.01	0.01
K2O	39	0.001	0.010	0.001	0.010	0.004	0.004	0.057	0.051	0.049	0.040	####	0.003	0.009	0.015	0.006
Sum		20.00	20.83	20.00	19.99	20.00	20.00	10.00	10.00	10.01	10.00	####	10.00	10.00	9.99	9.99
Li	7	2.9	59	2.4	8.6	6.4	8.5	11.8	0.6	8.8	12.1	<0.44	<0.10	<0.32	0.9	1.2
B	11	0.15	0.94	0.46	1.14	9.27	1.82	1.43	<1.50	1.95	1.84	2.69	<0.24	0.86	<1.62	<1.14
Cl	35	<22	800	40	<68	101	51	17400	15500	14000	12600	155	43	114	<179	<131
Cr	53	2890	1080	2840	2620	236	2340	96	<14	14	<13	<3	4	394	<4	<3
As	75	<0.02	64	0.1	<0.06	1.2	0.2	28	55	55	10	26	38	13	31	27
Rb	85	0.02	1.13	<0.005	0.41	0.12	0.18	12	9	11	12	0.25	0.08	0.39	0.50	0.14
Sr	88	0.03	8.96	0.05	0.91	0.99	0.34	350	220	330	340	<0.04	0.09	<0.03	0.18	<0.04
Y	89	2.40	4.11	3.19	1.96	1.58	1.94	0.11	0.09	0.06	0.04	####	0.027	0.066	<0.040	<0.037
Zr	90	2.77	<0.013	3.33	1.11	1.83	3.33	0.03	0.10	<0.03	0.07	<0.06	<0.01	0.04	0.08	<0.04
Nb	93	0.018	0.055	0.023	0.071	<0.009	<0.006	0.022	0.049	<0.02	0.114	####	0.255	0.125	0.792	0.077
Sb	121	0.01	0.14	0.02	<0.034	0.02	0.02	1.02	1.19	1.50	0.84	0.26	0.18	0.14	0.40	0.14
Cs	133	0.003	1.03	<0.002	0.022	0.014	0.027	12.7	8.3	11.6	10.8	####	0.014	0.068	0.087	0.038
Ba	137	<0.02	4.6	<0.02	0.8415	<0.04	0.149	320	220	290	270	<0.24	0.17	1.30	<0.32	<0.20
La	139	0.003	0.021	0.003	<0.006	0.053	0.007	1.25	0.59	1.05	0.94	<0.021	0.009	<0.020	<0.036	<0.028
Ce	140	0.007	<0.009	0.011	0.021	0.066	0.015	0.93	0.40	1.01	0.64	<0.025	0.011	0.027	0.063	<0.028
Nd	143	0.075	<0.06	0.083	<0.08	<0.04	0.176	0.187	0.196	0.179	<0.14	<0.17	<0.05	<0.11	<0.13	<0.14
Dy	163	0.38	0.53	0.55	<0.02	0.12	0.24	0.026	<0.064	<0.056	0.064	<0.07	<0.01	<0.04	<0.10	<0.07
Lu	175	0.045	0.021	0.061	0.047	<0.002	0.020	n.a.	n.a.	n.a.	n.a.	<0.016	<0.004	<0.010	<0.025	<0.015
Ta	181	<0.002	0.007	<0.001	<0.005	<0.002	<0.004	<0.004	<0.017	<0.006	<0.016	<0.010	0.011	<0.013	0.092	<0.023
Tl	205	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.28	0.12	0.23	0.18	n.a.	n.a.	n.a.	n.a.	n.a.
Pb	208	0.009	18.6	0.021	0.225	0.086	0.078	240	95	110	112	0.16	0.11	0.19	0.21	0.11
Th	232	<0.001	0.017	<0.001	<0.002	0.020	0.004	<0.001	<0.024	<0.011	<0.015	####	<0.004	0.055	<0.034	<0.017
U	238	<0.002	0.064	0.007	<0.005	0.058	0.013	0.202	0.028	0.142	0.060	<0.021	0.028	0.022	<0.023	<0.017

Notes:

Element oxides are given in wt.%, elements in µg/g

Concentrations set in bold were used as the internal standard for data reduction (see text for explanations)

Entries "< value" represent limits of detection calculated for each element in every inclusion individually (Halter et al., 2002) employing the stringent LOD calculation from Pettke et al. (2012)

n.a. = not available

Values set in italic are deemed outliers and are not considered further

Note that the concentrations for Tl are to be taken with caution because Tl in SRM610 is heterogeneously distributed (Eggins and Shelley, 2002; Tl = 60 µg/g was used here)