Carbonation of subduction-zone serpentinite (high-pressure ophi-carbonate; Ligurian Western Alps) and implications for the deep carbon cycling

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Abstract

Much of the long term carbon cycle in solid earth occurs in subduction zones, where processes of devolatilization, partial melting of carbonated rocks, and dissolution of carbonate minerals lead to the return of CO₂ to the atmosphere via volcanic degassing. Release of COH fluids from hydrous and carbonate minerals influences C recycling and magmatism at subduction zones. Contradictory interpretations exist regarding the retention/storage of C in subducting plates and in the forearc to subarc mantle. Several lines of evidence indicate mobility of C, of uncertain magnitude, in forearcs. A poorly constrained fraction of the 40-115 Mt/y of C initially subducted is released into fluids (by decarbonation and/or carbonate dissolution) and 18-43 Mt/y is returned at arc volcanoes. Current estimates suggest the amount of C released into subduction fluids is greater than that degassed at arc volcanoes: the imbalance could reflect C subduction into the deeper mantle, beyond subarc regions, or storage of C in forearc/subarc reservoirs.

We examine the fate of C in slab/interface ultramafic rocks, and by analogy serpentinitized mantle wedge, via study of fluid-rock evolution of marble and variably carbonated serpentinite in the Ligurian Alps. Based on petrography, major and trace element

concentrations, and carbonate C and O isotope compositions, we demonstrate that serpentinite dehydration at 2-2.5 GPa, 550°C released aqueous fluids triggering breakdown of dolomite in nearby marbles, thus releasing C into fluids. Carbonate + olivine veins document flow of COH fluids and that the interaction of these COH fluids with serpentinite led to the formation of high-*P* carbonated ultramafic-rock domains (high-*P* ophicarbonates). We estimate that this could result in the retention of ~0.5-2.0 Mt C/year in such rocks along subduction interfaces. As another means of C storage, 1 to 3 km-thick layers of serpentinitized forearc mantle wedge containing 50 modal % dolomite could sequester 1.62 to 4.85 Mt C/year.

We stress that lithologically complex interfaces could contain sites of both C release and C addition, further confounding estimates of net C loss at forearc and subarc depths. Sites of C retention, also including carbonate veins and graphite as reduced carbonate, could influence the transfer of slab C to at least the depths beneath volcanic fronts.

Keywords: Subduction; serpentinite; marble; aqueous carbonic fluids; deep Carbon cycle; high-pressure ophicarbonate

1. Introduction

In part due to the anthropogenic buildup of CO₂ in the atmosphere, geoscientists have devoted considerable attention to understanding not only CO₂ release by burning of fossil fuels, and natural and human-induced sequestration of atmospheric CO₂ storage in minerals, but also the full set of geologic processes governing long-term (up to 10⁹ yr) change in atmospheric CO₂ levels (Kerrick and Connolly, 1998; Jarrard, 2003; Kelemen and Matter, 2008; Dasgupta and Hirschmann, 2010; Reusch et al., 2011; Tumiati et al., 2012; Stagno et al., 2013; Dasgupta, 2013; Bebout, 2014). Much of the long-term cycling of C in the solid Earth occurs at

51 subduction zones, where carbonated rocks (and rocks containing organic C; Bebout, 2014) are
52 transported into the mantle and where devolatilization, melting, and dissolution of subducted
53 rocks leads to return of CO₂ to the atmosphere in arc volcanic gases (Berner et al., 1983;
54 recent discussion in Dasgupta, 2013; Collins et al., 2015; Kelemen and Manning, 2015). In
55 such environments, the interplay of carbonation and decarbonation of rocks exerts a major, if
56 not absolute, control on surface C emission and thus atmosphere evolution.

57 The deep C subduction cycle is still poorly understood, and a broad range of possibilities
58 exists regarding the residency of C in subducting plates and in the supra-subduction mantle
59 over wide ranges in pressure, temperature and fluid composition. The available experiments
60 and closed-system thermodynamic modeling of carbonated rocks (metasediments, altered
61 oceanic crust) document that carbonate minerals can remain stable to the very high pressures
62 and temperatures experienced in subduction zones, resulting in minimal C release to
63 subduction fluids in forearcs (Molina and Poli, 2000; Thomsen and Schmidt, 2007; Kerrick
64 and Connolly, 1998; 2001a; 2001b; Poli et al., 2009; Cook-Kollars et al., 2014; Collins et al.,
65 2015). Reduction of carbonate to graphite, related to fluid-rock interaction, also can affect the
66 degree of C retention to great depths in subducting rocks (Galvez et al., 2013). On the other
67 hand, much higher C solubility at subarc conditions (>700 °C; 2.5 GPa) has been proposed
68 (Caciagli and Manning, 2003; Gorman et al., 2006; Kelemen and Manning, 2015). Several
69 observations indicate significant C release from slabs at deep forearc and subarc depths, and
70 transport of this C into forearc mantle wedges (and overlying crust) where it can be stored.
71 These observations include (i) high CO₂ output from arc volcanoes, (ii) carbonic and diamond-
72 bearing fluid/melt inclusions in high- and ultrahigh-*P* rocks, (iii) hydrated-carbonated
73 assemblages in metasomatized peridotites from subducting plates and mantle wedges
74 (McInness and Cameron, 1994; Van Roermund et al., 2002; Stockhert et al., 2001; Sapienza et
75 al., 2006; Scambelluri et al., 2008, 2015; Frezzotti et al., 2011; Malaspina et al., 2009; Kelemen

76 and Manning, 2015). Thermodynamic modeling indicates release of C as CO₂ via
77 decarbonation of hydrated-carbonated rocks, in particular in situations where these rocks are
78 infiltrated by externally-derived H₂O-rich fluids (Gorman et al., 2006; Dolejs and Manning,
79 2010; Cook-Kollars et al., 2014; Collins et al., 2015; Kelemen and Manning, 2015). Also,
80 experimental work and studies of natural high- and ultrahigh-*P* rocks demonstrate that
81 carbonate can dissolve in aqueous fluids at forearc-to-subarc *P-T* conditions (Caciagli and
82 Manning, 2003; Dolejs and Manning, 2010; Sanchez-Valle, 2003; Frezzotti et al., 2011; Ague
83 and Nicolescu, 2014). Thus, there are multiple lines of evidence for the mobility of C in forearc
84 and subarc slab sections, but the magnitude of C loss by each of these mechanisms remains
85 highly uncertain (Poli et al. 2009; Ague and Nicolescu 2014; Cook-Collars et al. 2014; Collins
86 et al. 2015; Kelemen and Manning 2015). A poorly constrained fraction of the 40-115 Mt/year
87 C initially subducted is released into fluids and melts (by decarbonation, carbonate
88 dissolution, and partial melting) and 18-43 Mt/year is returned at arc volcanoes (see the
89 recent estimates by Collins et al., 2015; Kelemen and Manning 2015). The apparent imbalance
90 between the amounts of C delivered to subduction fluids and the smaller C return to the
91 atmosphere at arcs could reflect the subduction of C into the deeper mantle, or the storage of
92 (hidden) C in the forearc and subarc mantle, and in deep crustal reservoirs (see Sapienza et al.
93 2009; Collins et al., 2015; Kelemen and Manning, 2015).

94 A key open issue regards the fate of carbonic fluids when they interact with rocks other
95 than their sources (i.e., downstream from their sites of generation), particularly in slabs and
96 in supra-subduction serpentinitized mantle and depending on their *P-T* flow trajectories. For
97 example, abundant calcite/aragonite-bearing veins, and carbonated rocks in melange zones,
98 attest to the ability of C-bearing fluids to deposit carbonate along some fluid flow paths (see
99 Bebout, 1991; Kelemen and Manning, 2015; Bebout and Penniston-Dorland, 2016). Here we
100 examine the subduction-zone evolution of eclogitic serpentinite, marble and carbonated

serpentinite in the Voltri Massif (W. Alps, Italy). We show that the H₂O-rich fluid released by dehydration of serpentinite triggers decarbonation of nearby dolomitic marble, leading to C release into fluids. Abundant magnesite+olivine veins at this locality indicate the transport of an aqueous-carbonic fluid and we suggest that the interaction of this COH fluid with some of the serpentinite layers resulted in carbonation of silicate mineral assemblages and formation of a new class of rocks, identified here as high-*P* ophicarbonates. We discuss this finding in terms of fluid/rock interactions controlling the fate of C in the slab and in serpentinized supra-subduction mantle. We conclude that C fixed by such a mechanism into carbonate in slab and mantle wedge serpentinite would not be released from the subduction interface at the *P-T* conditions recorded in these rocks, and instead would remain at the base of the mantle wedge unless later released as a result of heating and/or decompression.

112

113 **2. Geological background**

The outcrops studied are in the Ligurian Voltri Massif, a high-*P*, blueschist- to eclogite-facies ophiolite at the SE end of the Italian W. Alps (**Fig. 1A**). The Voltri Massif largely consists of high-*P* serpentinite hosting eclogitic metagabbro, metarodingite and metabasalt, associated with high-*P* carbonate-bearing oceanic metasedimentary rocks (referred to as the Schistes Lustrés) interlayered with metabasalt and chert (Capponi and Crispini, 2002). The Erro-Tobbio (meta)peridotite Unit, recording pre-Alpine rifting and oceanization, followed by Alpine subduction, is tectonically coupled with the above rock units (Hoogerduijn Strating et al., 1983; Scambelluri et al., 1995).

Several petrologic studies have considered with the Alpine subduction-zone evolution of the Voltri Massif and most relevant to the present study are the *P-T* estimates of eclogites and associated serpentinite. The first rock-type develops garnet, omphacite and rutile at 450-500 °C and 1.3-1.7 GPa (Messiga and Scambelluri, 1991; Federico et al., 2004). The Voltri

126 serpentinite records a polyphase evolution, with initial low-grade chrysotile-lizardite
127 replaced by antigorite and then by olivine-bearing assemblages (Cimmino et al., 1979;
128 Scambelluri and Rampone, 1999). This evolution is comparable to that documented for the
129 Erro-Tobbio metaperidotite, recording transition from chrysotile/lizardite to antigorite
130 serpentine, followed by eclogite-facies dehydration to olivine + antigorite + Ti-clinohumite-
131 bearing assemblages (Scambelluri et al., 1995). This peak assemblage also occurs in vein
132 systems, collecting the aqueous subduction fluid released by serpentinite during
133 eclogitization (Scambelluri et al., 1995). Ages of peak metamorphism ranging from 45 to 34
134 My were estimated with $^{40}\text{Ar}/^{39}\text{Ar}$ and in-situ U/Pb isotopic systems, respectively (Federico
135 et al., 2006; Rubatto and Scambelluri, 2003). Prograde subduction evolution was followed by
136 retrograde blueschist- to greenschist- metamorphism related to exhumation (Messiga and
137 Scambelluri, 1991; Hermann et al., 2000). This evolution was accompanied by superposed
138 deformation episodes producing composite tectonic fabrics and isoclinal folding (Capponi and
139 Crispini, 2002). An evolution of the Voltri Massif along plate interface domains, where rock
140 slices of different provenance (slab and overlying mantle) and age are tectonically stacked
141 together, was recently proposed according to field, geochemical and numerical modeling
142 studies (Federico et al., 2007; Scambelluri and Tonarini, 2012; Malatesta et al., 2012).

143 All of the above studies focus on hydrated mafic-ultramafic systems, with little attention
144 paid to C-bearing lithologies, notably ophicarbonates. For decades (Cortesogno et al., 1980,
145 1981) these carbonated ultramafic rocks have been regarded as the high-*P* equivalents of
146 oceanic ophicarbonates from the non-subducted Northern Apennine ophiolites (Cortesogno
147 et al., 1980). The genesis of the Ligurian ophicarbonates is thought to be related to the
148 exposure of serpentized mantle peridotite on the Mesozoic Tethyan ocean floor and its
149 interaction with seawater (Cortesogno et al., 1980). The non-subducted Northern Apennine
150 ophicarbonates (Cortesogno et al., 1980) correspond to (i) chrysotile/lizardite serpentized

151 peridotite carbonated along hydrothermal fracture systems conveying seawater into the
152 fractured shallow mantle (Cortesogno et al., 1980). The Apennine ophicarbonates still
153 preserve oceanic stratigraphic contacts, showing direct transition to basaltic lava flows,
154 calcareous sediments and extensional tectonic breccias consisting of serpentinite and/or
155 gabbroic clasts with a micrite matrix.

156 The main occurrences in Voltri and in nearby blueschist-facies units are shown in **Figure**
157 **1A**. These rocks correspond to hundreds of meters-long and tens of meters-thick bodies of
158 carbonated serpentinite located between serpentinite and the metasedimentary cover of
159 oceanic crust. Ophicarbonates are in contact with, or grade into, high-*P* olivine + antigorite
160 serpentinite and consist of ultramafic rocks cut by veins and domains containing carbonate.
161 The high-*P* assemblage in ophicarbonate changes as a function of the local rock and fluid
162 composition: it generally consists of antigorite + carbonate and variable amounts of olivine,
163 diopside, andraditic garnet, tremolite, chlorite, opaque phases (Cortesogno et al., 1981). An
164 estimate of the high-*P* peak conditions for the Voltri ophicarbonate rocks is not yet available
165 and evidence of fluid/rock interaction in high-*P* carbonated serpentinite has not been
166 described, particularly regarding the stability/instability of carbonate in such complex natural
167 systems.

168

169 **3. Field occurrence**

170 The investigated rocks outcrop in the North-western Voltri Massif, along the Erro River, ca. 10
171 km north of the village of Sassello (GPS coordinates N44.55401, E8.44616). From top to
172 bottom, the rock sequence consists of dolomite marble ($\pm$ garnet) and serpentinite, separated
173 by an intermediate zone of hybrid rocks showing variable modal amounts of serpentine and
174 dolomite (**Fig. 1B**).

175 Serpentinite displays an antigorite foliation with olivine and Ti-clinohumite-rich layers.
176 Veins with olivine and Ti-clinohumite are embedded and deformed within the foliation that is
177 locally cut by late-stage carbonate-bearing veins. Marbles range from dolomite+garnet to
178 almost pure dolomite varieties. The garnet-bearing marble displays a coarse foliation that
179 envelops rounded, fist-sized, blocks of mafic eclogite (**Fig. 2A**). The garnet-dolomite foliation
180 in marble thus likely formed under high-*P* conditions. When garnet-marbles are outside the
181 main hybrid-rock horizon, garnet is coarse, idiomorphic and red in colour; when the garnet
182 marble is inside or at the margin of the hybrid-rock domain, garnet is irregular in shape and
183 green. Layers of dolomite (garnet-free) marble are only present inside the hybrid-rock
184 domain (**Fig. 2B**).

185 The hybrid-rocks are intermediate between serpentinite and marble: their mineral
186 composition is quite variable and ranges from marble (with or without green garnet), to
187 marble with increasing modal clinopyroxene and antigorite, to carbonated serpentinite. The
188 latter grades into pure serpentinite: this transition is well exposed in the southern part of the
189 outcrop (**Fig. 1B**). The hybrid rock domain displays the irregular alternation of transposed
190 carbonate-rich layers and of serpentine-rich layers (**Figs. 2B,C**). These features suggest
191 derivation of the hybrid-rocks either from mixing during deformation of the contact between
192 marble and serpentinite, or from an ophicarbonates horizon formed on the seafloor between
193 serpentinite and marble and then deformed during subduction. Importantly, the hybrid rocks
194 are cut by olivine+Ti-clinohumite veins and by several centimetre-thick veins with magnesite
195 and olivine (**Figs. 2D,E**). The veins are folded by the dominant foliation, which implies that
196 veining occurred early in the deformation history of this suite of rocks.

197 The above rocks all display four superposed stages of ductile deformation. In serpentinite,
198 the earliest stages forms a composite fabric (D1+D2) that affects a pristine antigorite foliation,
199 an olivine+Ti-clinohumite+diopside+antigorite foliation, and the olivine veins. The same

200 fabric in hybrid rocks causes transposition of carbonate-rich and of serpentinite-rich layers
201 and folding of olivine-bearing fabrics and of olivine + carbonate veins. In the dolomite +
202 garnet marble, stages D1 and D2 produced the garnet-dolomite foliation that includes the
203 eclogite rounded clasts and that parallels the foliation inside the eclogite blocks (**Fig. 2A**). A
204 third event causes further folding of the sequence and of the early D1+D2 structures and veins
205 (**Fig. 2D**). The latest D4 stage produces a crenulation with a vertical axial plane. The olivine-
206 and carbonate-bearing structures in serpentinite and hybrid rocks represent early peak
207 evolutionary stages recorded by the whole sequence.

208

209 **4. Petrography**

210 **4.1 (Red) Garnet Marble**

211 These rocks contain dolomite, garnet, clinopyroxene, chlorite, calcite and opaque minerals.
212 They display coarse and zoned garnet porphyroblasts, with dusty polycrystalline cores and
213 clear rims. This garnet (grt1) contains inclusions of calcite, dolomite, chlorite and
214 clinopyroxene, and is in equilibrium with coarse dolomite and clinopyroxene forming the rock
215 matrix (**Fig. 3A**). Dolomite is the main matrix mineral oriented along the foliation enveloping
216 the mafic eclogitic clasts (**Fig. 2A**). The rock matrix also contains neoblastic, finer-grained,
217 garnet (grt2), dolomite (dol2) and clinopyroxene (cpx2), representing a recrystallization
218 stage of the marble. The second paragenesis occurs along thin sheared microdomains cutting
219 thorough the rock. The last paragenesis recognized is composed of calcite and tremolite.

220 This type of red garnet-bearing marble outcrops outside the hybrid rock horizon (see **Fig.**
221 **1B**); the margins and the internal part of the hybrid domain contain green garnet-bearing
222 marble and pure dolomite marble (see later section on hybrid rocks).

223 **4.2 Serpentinite**

224 In this rock, the D1+D2 antigorite foliation wraps around microlithons of earlier antigorite.
225 This foliation deforms layers and/or veins with olivine, Ti-clinohumite, diopside: these
226 minerals texturally coexist with antigorite in the same paragenesis along the main composite
227 high-*P* foliation (**Fig. 3B**). This structure similar to what is observed in other Voltri and Erro-
228 Tobbio areas (Scambelluri et al., 1995). Comparable olivine deformation structures along the
229 D1+D2 foliation are also present in the serpentine-rich hybrid rocks (see below). The late-
230 stage crystallization of post kinematic antigorite indicates rock-reequilibration during
231 retrograde metamorphism.

232 **4.3 Hybrid-rocks**

233 This rock type is quite heterogeneous and consists of the intercalation of carbonate- and
234 serpentine-rich layers. Hereafter, the two main lithologies are presented separately.

235 *Marble (with diopside $\pm$ green garnet)*

236 This rock either consists of deformed green garnet+dolomite-bearing assemblages, or of pure
237 dolomite layers, free of associated quartz and silicate minerals. In the first case, garnet is
238 macroscopically green in color and the rock structure and mineralogy are comparable to the
239 previously discussed red-garnet marble. In the hybrid rock zone garnet is less abundant; the
240 coarse garnet contains inclusions of dolomite, chlorite and clinopyroxene and its rims are
241 frequently overgrown by clinopyroxene, calcite, chlorite and Fe-oxide. Some marble layers
242 within the hybrid rock horizon show irregular patches of diopside+dolomite+Fe-oxide
243 interpreted as pseudomorphs after the green garnet. Coarse dolomite in these rocks was in
244 equilibrium with coarse garnet, and became progressively porphyroclastic and involved in
245 deformation.

246 The garnet-bearing and the pure dolomite marbles in the hybrid horizon display a
247 dominant foliation enveloping porphyroclastic dolomite (**Fig. 3C**). The porphyroclastic
248 dolomite is present as single coarse crystals or polycrystalline, quartz-free, aggregates

249 flattened and deformed along the main foliation. Coarse dolomite crystals have subgrains with
250 well developed twinning (**Fig. 3C**). In all hybrid samples, porphyroclastic dolomite is replaced
251 by syn-tectonic layers of oriented diopside crystals (same as in **Fig. 3C**). Coarser diopside
252 parallel to the main foliation replaces the inner deformed portions of the porphyroclastic
253 dolomite layers along grain boundaries. The foliated pure diopside layers clearly replace
254 dolomite and become volumetrically abundant in the most deformed rock domains (Fig. 3C):
255 here diopside is locally replaced by interstitial retrograde tremolite+calcite.

256 *Hybrid carbonate-bearing serpentinite (high-P ophicarbonate)*

257 As for the associated marbles, these hybrid rocks are quite heterogeneous in texture and in
258 modal abundance of the rock-forming minerals. In general, the carbonated hybrid
259 serpentinite contains antigorite, dolomite, diopside, chlorite, oxides and variable amounts of
260 metamorphic olivine and Ti-clinohumite. Some hybrid serpentinite layers correspond to
261 antigorite schists in which olivine and Ti-clinohumite veins are dismembered along the main
262 foliation and texturally equilibrate with antigorite and dolomite. Some other layers consist of
263 foliated antigorite alternating with domains of porphyroclastic dolomite (same as in marbles,
264 **Fig. 3C**), which may derive from tectonic transposition of serpentinite and dolomite marbles.
265 In such cases the serpentinite layers show development of high-*P* olivine and Ti-clinohumite,
266 the dolomite layers show porphyroclastic dolomite replaced by syn-tectonic diopside (e.g.,
267 **Fig. 3C**). In all hybrid carbonated serpentinites neoblastic dolomite developed at the expense
268 of high-*P* olivine, diopside, Ti-clinohumite and antigorite (**Figs. 3D,E**). In practice, after
269 formation of high-*P* olivine-assemblages in serpentinite and after replacement of dolomite by
270 diopside in marbles, the various silicate minerals in serpentinites are overgrown by
271 neoblastic dolomite. This feature is shown in **Figures 3C and 3D**, where metamorphic olivine
272 and diopside (forming the high-*P* serpentinite assemblage and the replacement of
273 porphyroclastic dolomite, respectively) are overgrown by fine-grained non-twinned dolomite.

274 In some samples this carbonation effect becomes dominant and the rock transforms into a
275 dolomite-antigorite-bearing serpentinite, where the high-*P* olivine tends to recrystallize and
276 texturally equilibrate with the replacive, non-twinned, neoblastic dolomite (**Fig. 3F**). In such
277 samples, formation of up to 40-50% modal neoblastic dolomite transforms the former
278 serpentinite into a subduction zone rock in which carbonate minerals form during eclogite-
279 facies metamorphism. These rocks are here defined as high-*P* ophicarbonates.

280 *Olivine-carbonate veins*

281 These veins contain magnesite, dolomite, calcite, chlorite, olivine, oxides and serpentine. A
282 first relict assemblage consists of coarse magnesite associated with chlorite, oxide and olivine.
283 Olivine is well preserved in a few cases and is mostly overgrown by dolomite and/or by
284 retrograde very fine-grained serpentine. Magnesite is well preserved and shows concentric
285 zoning: it is replaced by a first generation of dolomite along recrystallized domains and along
286 the rims, and by a second generation of calcite that replaces magnesite and dolomite along the
287 outer rims of the vein carbonates (Repository File R1).

288

289 **5. Analytical Methods**

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291 ***5.1. Bulk-rock and mineral major element analysis***

292 Bulk rock major element analyses were performed at the Actlabs Ltd. with X-ray fluorescence
293 (XRF) on powder pellets. Accuracy and precision are estimated as better than 3% for Si, Ti, Fe,
294 Ca and K and 7% for Mg, Al, Ms, and Na. Loss of ignition (LOI) was determined by weight
295 difference following ignition of samples in a furnace.

296 Major element mineral compositions were measured by electron microprobe analyses at
297 the Departement of Earth Science, University of Milano (Italy), using a JOEL Superprobe 8200.
298 We use a WDS system at 15.0 kV and 60 nA for the electron beam with a point analysis of 1

micron of amplitude and of 3 micron for mica minerals. The standards used were from natural silicates: Mg on olivine 153, Fe on fayalite 143, Na on omphacite 154, Ti on ilmenite, Mn on rodonite, K on K-feldspar 113, Al and Ca on anorthite 137, Si on wollastonite and Cr on metallic/pure Cr.

Scanning electron microscope microstructural analysis of rocks and analysis of some major element mineral compositions were made at the University of Genova (Italy) using a Philips SEM-515 with an accelerating potential of 15.0 kV and 20 nA.

5.2. Carbon and oxygen isotope analysis

Carbonate from various textural settings was sampled by micro-drilling using 1 and 2 mm diameter tungsten carbide bits. The samples were analyzed on a Finnigan MAT-252 using a GasBench II and the methods described by Collins et al. (2015). All samples were reacted with 0.2 ml. Phosphoric acid at 72°C for 6 hours to release CO₂ from all carbonate minerals (dolomite and, where present, magnesite and calcite). Unknowns were evenly spaced with analyses of a synthetic in-house carbonate standard and international standards NBS-18 and NBS-19. All samples were measured with six replicates following five reference gas peaks. Regular analysis of a house standard and international standard NBS-19 allowed monitoring and correction of the data, resulting in a standard deviation (1 σ) of ~0.2‰ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported relative to VPDB and VSMOW, respectively.

5.3 Pseudosection modeling

Pseudosection calculations were performed in the system CaO-FeO-Fe₂O₃-MgO-Al₂O₃-SiO₂-H₂O-CO₂ (CO₂-CFMASH) using the Perple_X software (version 6.7.1; Connolly, 2005) together with the Holland and Powell (1998) database and internally consistent solid solution models for olivine, orthopyroxene, clinopyroxene, chlorite, garnet, spinel, tremolite and dolomite-

ankerite (Franzolin et al., 2011). Antigorite, aragonite, talc and brucite were taken to be pure. The $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ ratio of bulk-rock compositions was not measured and was arbitrarily set to 0.5, a value consistent with the redox state of subduction serpentinites (Debret et al., 2014). A compensated Redlich-Kwong equation of state (Holland and Powell, 1991) was adopted to model the thermodynamic behaviour of H_2O - CO_2 fluids. This equation provides fluid density values (1.167 g/cm^3 at $5550 \text{ }^\circ\text{C}$ - 2 GPa) quite comparable to densities achieved using the recently proposed model of the dielectric constant of H_2O to 6 GPa (1.147 g/cm^3 ; Sverjensky et al., 2014). Thermodynamic properties of dolomite, rather than the assumptions made on bulk-rock chemistry and fluid equation of state, turn out to appreciably affect pseudosection topology. In our calculations we adopted the thermodynamic solid solution model of Franzolin et al. (2011) to better account for Ca-Mg-Fe ternary mixing and order/disorder phenomena, which may have relevant effects on the energetics of dolomite. This model, which is suitable up to P - T conditions of $\sim 6 \text{ GPa}$ and 1200 - $1300 \text{ }^\circ\text{C}$ (largely compatible with our estimated metamorphic peak conditions), is based on a van Laar macroscopic formalism and is able to reproduce the non-ideal mixing behaviour of ternary CaCO_3 - MgCO_3 - FeCO_3 carbonates by introducing two intermediate ordered components (namely ordered dolomite and dolomite₅₀ankerite₅₀) besides the usual calcite, magnesite and siderite end-members as in Holland and Powell (1998). The degree of ordering is given by the internal equilibrium reaction

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for which the enthalpy of formation ($\Delta H_{\text{R}}^{\text{dolomite}}$) is assessed in order to fit experimental phase relations. Holland and Powell (2003) preliminarily set $\Delta H_{\text{R}}^{\text{dolomite}}$ to -13.5 kJ/mol , while Franzolin et al. (2011) changed this value to -1 kJ/mol . In our thermodynamic modeling we

349 tried to avoid any semi-empirical assumption about the enthalpy of formation of ordered
350 dolomite by setting $\Delta H_R^{\text{dolomite}} = -5.74 \text{ kJ/mol}$ which is the value measured by solution
351 calorimetry (Navrotsky and Capobianco, 1987). The resulting pseudosection displays
352 calculated phase proportions and mineral compositions in excellent agreement with observed
353 mineral chemistry and petrographic evidence.

354

355 **6. Analytical results**

356 ***6.1. Bulk-rock and mineral compositions***

357 The major element whole-rock compositions of samples collected along a traverse from
358 serpentinite to marble (see **Fig. 1** for sample locations) are reported in **Repository Table R1**.
359 Besides the pure serpentinite and marble end-members, the analyzed sample set includes
360 hybrid rocks, ranging from carbonate-rich to serpentine-rich, in one part of the La Pesca
361 exposure (see **Fig. 1B**).

362 The whole-rock concentrations of SiO_2 , MgO , CaO , LOI , MnO , and Cr_2O_3 plot along linear
363 arrays (**Fig. 4**), reflecting increasing CaO added to serpentinite and $\text{MgO} + \text{SiO}_2$ added to
364 marble during tectonic mixing and chemical exchange between serpentinite and marble
365 within the hybrid-rock layer.

366 The major element compositions of the main rock-forming minerals are shown in
367 **Repository Table R2**. **Figure 5** shows the compositional variation of high-P olivine,
368 clinopyroxene and garnet from pure serpentinite outside the hybrid rock domain and from
369 carbonate-bearing serpentinite in the hybrid domain. In general, olivine and clinopyroxene
370 from the hybrid serpentinite have higher Mg and lower Fe with respect to olivine and
371 clinopyroxene from pure serpentinite (**Fig. 5**). The same relationship is observed for
372 antigorite. Clinopyroxene in the hybrid serpentinite is also richer in Mg and Ca than
373 clinopyroxene from garnet marble outside the hybrid domain. The red garnet from marbles

374 outside the hybrid domain shows large variability in andradite component (40 to 70%): this
375 component is higher (80% andradite) and quite homogeneous in green garnet from marble
376 inside the hybrid zone (**Fig. 5**). The increased andradite component of green garnet suggests
377 major Fe^{3+} changes possibly driven by oxydizing fluids circulating within the deformed hybrid
378 rock domain.

379

380 **6.2. Bulk-rock carbon and oxygen isotope compositions**

381 Carbon and O isotope compositions of carbonate in serpentinite, marble and hybrid
382 ophicarbonate rocks from La Pesca are presented in **Table 1** and **Figure 6**. Serpentinite
383 samples external to the hybrid zone, unaffected by intense carbonation, have $\delta^{13}\text{C}$ in the range
384 of -9.1 and -4.5‰; $\delta^{18}\text{O}$ ranges from +21.7 to +22.2‰. The red garnet marbles have $\delta^{13}\text{C}$ in
385 the range of +1.3 to +1.8‰ and $\delta^{18}\text{O}$ values of about +14‰. Values of the hybrid rocks
386 forming the main transposed layer in between serpentinite and marbles have variable O and
387 C isotopic compositions. Hybrid carbonate-bearing serpentine (high-pressure ophicarbonate)
388 display $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of -0.4 to +1.6 and of +12.7 to +14.9‰, respectively. Green garnet- and
389 diopside-bearing marbles from the hybrid zone have $\delta^{13}\text{C}$ of +0.6 to +1.9‰ and $\delta^{18}\text{O}$ from
390 +11.5 to +18‰, with the diopside-marbles plotting close to the serpentinite-carbonate
391 mixing curve (**Fig. 6A**). The lowest $\delta^{13}\text{C}$ values are for metamorphic carbonate veins inside
392 the hybrid serpentinites: vein carbonate has $\delta^{13}\text{C}$ of -2.6 to +0.7‰ and $\delta^{18}\text{O}$ of +12 to 22‰.
393 Exchange of the hybrid rocks domain with the fluids that crystallized metamorphic carbonate
394 veins could have produced the trend shown in **Figure 6A**, as such mixing could have
395 produced $\delta^{18}\text{O}$ values for the hybrid serpentinite lower than those of the possible pure marble
396 mixing endmember (for the the latter, an average $\delta^{18}\text{O}$ of +16‰).

397 The plot of $\delta^{13}\text{C}$ versus total carbonate content of the La Pesca rocks (**Fig. 6B**) shows no
398 valid statistical correlation between the extent of carbonation and the C isotope composition.

399 The diagram shows a jump in $\delta^{13}\text{C}$ values from pure serpentinite to the range for all the other
400 carbonate-bearing rocks and veins, the latter displaying $\delta^{13}\text{C}$ from -0.4 to +1.9‰. The $\delta^{18}\text{O}$
401 compositions show a similar relationship (**Tab. 1**), with only one carbonate vein having $\delta^{18}\text{O}$
402 comparable to that of pure serpentinite (**Fig. 6A**)

403

404 **7. Discussion**

405 ***7.1. Coupled devolatilization reactions and serpentinite carbonation***

406 The interlayered hybrid marble and serpentinite (**Fig. 1A**) presented here derive from
407 shearing/mechanical mixing of either a serpentinite-marble contact or, alternatively, of an
408 oceanic ophicarbonat horizon. Like in several modern settings, in the Alpine domain
409 peridotite serpentinization and deposition of the marble protolith occurred in an oceanic
410 environment, after exposure and hydration of mantle rocks near the seafloor (Cortesogno et
411 al., 1980; Lagabriele, 2009). At this stage, the marble with eclogite pods likely was a breccia
412 of mafic clasts in a carbonate matrix, as documented for extensional structures in the
413 Apennine, and as previously proposed for La Pesca (Cortesogno et al., 1980). Subduction-zone
414 metamorphism transformed the mafic clasts into eclogite, the matrix into garnet-dolomite
415 marble, and the oceanic serpentinite into olivine + Ti-clinohumite-bearing high-*P* serpentinite.

416 As mentioned above, the studied serpentinite underwent partial dehydration to olivine, a
417 process documented in Alpine high-*P* serpentinite (Scambelluri et al., 1995) and accompanied
418 by fluid drainage into vein systems with crystallization of carbonate-free, hydrous silicate
419 assemblages (**Fig. 3B**). The intriguing aspect of the serpentinite-carbonate system at La Pesca
420 is that the formation of eclogite-facies carbonate-free, olivine-bearing parageneses in
421 serpentinite was roughly coeval with dolomite replacement by diopside in marbles (**Fig. 3C**).
422 These coupled dehydration and decarbonation events thus enable to investigate formation
423 and behavior of COH subduction fluids.

424 The hypothesized fluid exchange among serpentinite and marble layers and the related
425 variation in fluid composition are sketched in **Figure 7**. The aqueous fluid released by
426 serpentinites could have carried aqueous silica, driving the reaction $\text{dolomite} + \text{SiO}_{2(\text{aq})} =$
427 $\text{diopside} + \text{CO}_2$ (**Fig. 7A**). Alternatively, the aqueous fluid enhanced carbonate dissolution, as
428 documented by experiments and by studies of natural rocks and fluids (Caciagli and Manning,
429 2003; Ague and Nicolescu, 2014; Kelemen and Manning, 2015). Dolomite breakdown and CO_2
430 release to the fluid may have shifted the fluid composition from H_2O -rich to a more mixed
431 COH-fluid. Interaction of the COH-fluid with the olivine-bearing high- P serpentinite led to
432 carbonation of the silicate mineral assemblage and to COH-fluid drainage into carbonate +
433 olivine veins (**Figs. 2E, 3D-F, 7B**). This process produced high- P ophicarbonate, where
434 carbonate minerals crystallize during subduction-zone, eclogite-facies interaction of COH-
435 fluid with ultramafic rocks. These rocks can therefore represent hidden C sinks in the slab or
436 in the supra-subduction mantle (see discussion below).

437 Fluid exchange behaviour among the various layers is also suggested by the major
438 element compositions and by the C-O isotopic compositions of rocks exposed at La Pesca
439 (**Repository Table R. 1**). The linear trends of major element (bulk-rock and mineral)
440 variation shown in **Figures 4** and **5** indicate that the associated ultramafic and carbonatic
441 systems might have exchanged components, as a result of mechanical mixing, perhaps
442 coupled with chemical diffusion and/or fluid/rock reaction, during subduction-zone
443 recrystallization. Increase in the andradite component of the green garnet from marbles of the
444 hybrid zone (**Fig. 5**) suggests circulation of an oxydizing fluid that caused an increase of the
445 Fe^{3+} content of coexisting garnet. Open-system behavior is also suggested by C and O isotope
446 compositions (**Fig. 6A**), showing that many of the hybrid carbonated serpentinite and of the
447 diopside $\pm$ green garnet marbles plot between pure serpentinite and pure marble, down to the
448 low $\delta^{18}\text{O}$ values pertaining to metamorphic carbonate-olivine veins (lower than that of the

449 marble end member). This suggests that the high-*P* ophicarbonate rocks at La Pesca were
450 likely affected by (serpentinite-derived?) fluids that infiltrated and exchanged with the
451 carbonate-bearing lithologies.

452

453 ***7.2. Estimates of peak metamorphism and of serpentinite carbonation***

454 The peak *P-T* conditions achieved during subduction of the serpentinite and hybrid
455 carbonated serpentinite are shown in **Figure 8** (red stars). The diagrams were computed with
456 the software Perple_X adopting the bulk-rock compositions of the serpentinite LPM09-04 and
457 of the hybrid sample LPD09-16D (**Repository Table R1**; see **Section 5.3** for details on the
458 bulk chemical systems and for parameters used for calculations).

459 In the carbonate-free serpentinite LPM09-04 (**Fig. 8A**) the peak olivine+antigorite+
460 diopside+chlorite paragenesis crystallizes at 500-600 °C through the olivine-forming reaction
461 antigorite+brucite = olivine+H₂O. The reaction liberates ~2 wt.% H₂O (Scambelluri et al.,
462 2004) and produces olivine-bearing assemblages in the serpentinite and in vein systems
463 hosted by this rock-type. The subduction-zone gradients recently proposed by Syracuse et al.
464 (2010; thin grey lines in **Fig. 8A**) are between 2-2.5 GPa for corresponding temperatures of
465 500-600 °C. Similar estimates can be calculated for the hybrid carbonated serpentinite
466 LPD09-16D (**Fig. 8B**), which contains the paragenesis olivine + antigorite + diopside +
467 dolomite + chlorite + COH-fluid, formed at 500-600 °C and 2-2.5 GPa along the subduction
468 gradients of Fig. 8A (Syracuse et al., 2010). Such conditions are comparable to those proposed
469 so far for other Voltri serpentinites (Scambelluri and Rampone, 1999; Cimmino et al., 1989)
470 and for the nearby Erro-Tobbio serpentinitized peridotite unit (Scambelluri et al., 1995). At
471 such conditions Ti-clinohumite is stable in the Voltri and Erro-Tobbio serpentinites (Cimmino
472 et al., 1979; Scambelluri et al., 1995), analogous to what is observed at La Pesca. We thus
473 assume 2-2.5 GPa and *T* greater than 500 °C as the peak conditions achieved during

474 subduction of the La Pesca rock package.

475 At 500 °C, the La Pesca serpentinite thus underwent dehydration and production of
476 carbonate-free vein systems hosting hydrous silicate phases (olivine, Ti-clinohumite, chlorite,
477 antigorite). Interaction of the released aqueous fluid with dolomite-bearing rock layers
478 produced the diopside replacement after dolomite and release of CO₂ to the fluid (**Figs. 3C, 7**).
479 This aqueous-carbonic fluid could have produced the carbonate + olivine-bearing veins in the
480 hybrid rock layers (**Figs. 2E,F**).

481 The effect of the COH-fluid in serpentinite is shown in the H₂O-CO₂ section of **Figure 8C**.
482 The diagram is computed for the carbonated serpentinite sample LPD09-16D and a COH fluid
483 composition (see **Section 5.3** for details of the calculation): it shows the mineral assemblages
484 forming in the hybrid serpentinite at fixed pressure-temperature conditions (2 GPa, 550 °C)
485 and changing bulk concentrations of CO₂ and H₂O. The peak assemblage antigorite + olivine +
486 diopside + chlorite + dolomite + COH-fluid requires minimum bulk water contents of 5wt%.
487 Based on the measured 12wt.% LOI and on the 30% modal dolomite of sample LPD09-16D,
488 about 3wt.% bulk-rock CO₂ can be estimated. The modal contents of olivine and diopside in
489 the sample decrease with increasing CO₂ content (**Fig. 8C**), implying that the CO₂ released by
490 dolomite decarbonation gets fixed via carbonation of the serpentinite silicate assemblage.
491 Pseudosection modelling of hybrid serpentinite thus confirms the petrographic finding of
492 peak metamorphic olivine, diopside and antigorite progressively overgrown by neoblastic
493 (untwinned) dolomite (**Figs. 3D,E**). The process leads to serpentinite carbonation within and
494 around the hybrid zone with formation of high-*P* ophicarbonates.

495

496 ***7.3. Large-scale implications and carbon storage in subduction-zone serpentinite***

497 The high-*P* Voltri Massif represents a fossil plate-interface domain that was exhumed from
498 subduction-zone depths to the surface. Therefore, the high-*P* ophicarbonates described here

499 have implications for C cycling on a larger scale. Rocks similar to the hybrid lithologies
500 described in this paper could enable C storage within subducting plates, in the overlying
501 mantle and in plate interface environments in which sediments, oceanic crust and mantle are
502 tectonically juxtaposed. In all three of these regions, serpentinitized ultramafic rocks can be
503 widespread and fluid-mediated chemical exchange and the interplay of dehydration-
504 decarbonation reactions could be maximized (see Bebout and Penniston-Dorland, 2016). In
505 this context, C storage in neoblastic, high-*P* carbonate minerals in serpentinite impacts the
506 large-scale C subduction cycle (mostly forearc domains). The sketch portrayed in **Figure 9**
507 shows a sequence of H₂O and C reservoirs in subduction zones, mostly serpentinite and
508 associated carbonate-bearing rocks. Serpentinite dehydration under high-*P/T* conditions and
509 release of H₂O-rich fluids represents the initial reaction and the engine producing mobile
510 fluids free driving to decarbonation or carbonate dissolution in carbonate-rich reservoirs (as
511 on Syros; Ague and Nicolescu, 2013). As shown here, the COH-fluid produced by such
512 interplay of dehydration-decarbonation reactions is very reactive with the silicate phases in
513 the high-*P* serpentinite, driving to carbonation of olivine and clinopyroxene (see **Fig. 3D,E** for
514 a fluid with 3 wt% CO₂). Once olivine and diopside are exhausted, continued flushing by the
515 COH-fluid will lead to antigorite carbonation and crystallization of up to 40-50% modal
516 carbonate in the ultramafic rocks. Formation of high-*P* ophicarbonate in serpentinitized
517 ultramafic rocks from slab, plate interface and supra-subduction mantle environments thus
518 leads to storage of 25wt.% CO₂ in the rock. In an attempt to estimate the amount of C
519 potentially stored in a top-slab rock package similar to La Pesca, we consider (based on field
520 evidence; see **Fig. 1B**) a layer consisting of high-*P* ophicarbonate (hybrid carbonated
521 serpentine; 67 vol.%) and garnet marbles (33 vol.%). We hypothesize that such layers may
522 extend continuously for several kilometers down dip, extending along the entire global strike
523 length of subduction zones and ranging from 300 m to 1 km in thickness. The input

parameters used for this mass balance estimate (**Repository File R3**) are the same as those employed by Kelemen and Manning (2015). Average mineralogical compositions are 50-60 wt.% antigorite and 40-50 wt.% dolomite for high-*P* ophicarbonates, and 75 wt.% dolomite plus 25 wt.% garnet for marbles. Densities of 2.84 g/cm³ for dolomite, 2.73 g/cm³ for antigorite, and 3.60 g/cm³ for garnet (Deer et al., 2013) are adopted in this calculation. By changing the assumed thickness and modal mineralogical composition of ophicarbonate rocks within their limits, we obtain minimum and maximum values for C transfer of 0.52-0.58 and 1.72-1.94 Mt C/year, respectively. Considering the estimate of maximum release of 66 Mt C/year from the slab (Kelemen and Manning, 2015, and references therein), storage of ~0.5-2.0 Mt C/year in high-*P*, ophicarbonated serpentinite is regarded as an important part of the global C budget. Alternatively, another large reservoir favorable for storage of C extracted from COH slab fluids is represented by the serpentinized mantle wedge, where the thickness of serpentinite layers is estimated on the order of 1 to 3 km and locally up to 10 km (Bostock et al., 2002; Nikulin et al., 2009; Kawakatsu and Watada, 2007; Guillot et al., 2015). In such cases, considering formation of 50 modal % dolomite in a 1 to 3 km-thick layer of serpentinized forarc mantle, the amount of C stored increases up to 1.62 to 4.85 Mt C/year (**Repository File R3**). And, lithological layers of high-*P* ophicarbonate, similar to those at La Pesca, could form within the shallow mantle thermal boundary layer beneath arcs and backarcs, where COH-fluids exsolved from, cooling crystallizing magmas interact with mantle peridotite, as proposed by Kelemen & Manning (2015).

As other examples of carbonation of ultramafic rock during subduction-zone metamorphism, lawsonite-blueschist-facies mélange matrix in the Catalina Schist (exposed on Santa Catalina Island, California) in some areas contains relatively minor carbonate (see Bebout, 1991; Bebout and Barton, 1993; Kelemen and Manning, 2015). This carbonate was likely incorporated as a result of fluid-rock interactions and has $\delta^{18}\text{O}$ consistent with

549 equilibration with the metamorphic fluids affecting this unit on a regional scale (Bebout,
550 1991). In the amphibolite-facies mélange unit in the Catalina Schist, some ultramafic rocks
551 metasomatized during high-*P* metamorphism contain ankeritic dolomite ascribed to
552 interaction with COH fluids released from devolatilizing graphite-bearing metasedimentary
553 rocks elsewhere in the Catalina paleo-subduction zone (see Bebout and Barton, 1993). This
554 dolomite has $\delta^{13}\text{C}$ of -10 to -9‰ consistent with equilibrium at peak metamorphic
555 temperatures of 650-750°C with CO₂ with $\delta^{13}\text{C}$ of - 8 to - 7‰ similar to that calculated for
556 CO₂ in equilibrium with calcite-bearing veins and mélange matrix in the lawsonite-blueschist
557 unit. Taken together, these observations seemingly reflect release of C from devolatilizing
558 rocks (largely metasedimentary), and km-scale transport of this C, followed by its uptake by
559 ultramafic rocks along fluid flow paths.

560 Further study of the mobilization of C in deeply subducting oceanic lithosphere and
561 sediments, and along the lithologically complex subduction interface, should consider the full
562 range of processes not only liberating C into metamorphic fluids but also resulting in uptake
563 of C along the flow paths of these fluids. Carbonation of mantle peridotite and serpentinite,
564 within subducting plates, within the subduction interface zone, within the forearc mantle, and
565 in the shallow mantle thermal boundary layer beneath arcs and back arcs, via the processes
566 we have documented at La Pesca could produce hidden reservoirs in subduction zones
567 explaining the imbalance between C released from slabs and C erupted at arcs. Our work
568 therefore provides field-based petrologic evidence and quantitative constraints to the similar
569 hypothesis previously provided by Kelemen & Manning (2015) on the basis subduction
570 carbon fluxes.

571

572 **8. Conclusions**

573 We show that serpentinite plays a pivotal role in the subduction-zone carbon cycling. On

574 the one hand, de-serpentinization releases H₂O-rich fluid and supplies water to adjacent
575 carbonate-bearing rocks, promoting C mobility via enhanced decarbonation and carbonate
576 dissolution. On the other hand, reaction of serpentinite with COH-fluids converts silicate
577 minerals to carbonate minerals, thus sequestering C from the circulating aqueous-carbonic
578 fluid. This mechanism explains the apparent imbalance between the amount of C released
579 from subducting oceanic plates and sediment, and the amount that is returned to the
580 atmosphere at volcanic arcs.

581

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588

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807

808 **Figure captions**

809

810 **Figure 1. (A)** Geological map of the Voltri Massif. The red stars indicate the main outcrops of
811 subducted, high-*P*, oceanic ophiocarbonate. The studied area corresponds to the westernmost
812 star in the Northern sector of the map. **(B)** Field map of the studied garnet marble,
813 serpentinite and interposed hybrid rocks.

814

815 **Figure 2. (A)** Red garnet-bearing marble. This marble contains pods of mafic eclogite whose
816 internal garnet-clinopyroxene foliation, parallels the garnet-dolomite foliation in the marble.
817 **(B)** Hybrid rock domain showing the intercalation of pure dolomite marble and carbonated
818 serpentinite. **(C)** Fine centimetric layering of marble (pure dolomite marble and green garnet-
819 bearing marble) and carbonated serpentinite. **(D)** Deformed magnesite $\pm$ olivine vein in the
820 hybrid rock domain. **(E)** Close up of a coarse (mt-long) vein with magnesite and altered
821 olivine.

822

823 **Figure 3.** Photomicrographs showing the (red) garnet – dolomite marble **(A)** and the
824 olivine+antigorite+ Ti-clinohumite (pure) high-*P* serpentinite outside the hybrid rock domain
825 **(B).** **(C)** Dolomite marble within the hybrid rock domain. The marble contains no pristine
826 silicate minerals. It shows porphyroclasts of twinned (early) dolomite being replaced by
827 diopside along major foliation and deformation domains. **(D)** Hybrid high pressure
828 serpentinite showing high-pressure metamorphic olivine being replaced by neoblastic (non
829 twinned) dolomite. **(E)** Hybrid high-*P* serpentinite showing high-*P* metamorphic diopside
830 being replaced by neoblastic (non twinned) dolomite. **(F)** high-*P* metamorphic olivine
831 equilibrated with dolomite. **(D), (E)** and **(F)** show typical textures of high-pressure

832 ophicarbonates.

833

834 **Figure 4.** Bulk-rock composition of the rock-suite from La Pesca.

835

836 **Figure 5.** Compositions of major rock-forming minerals from La Pesca.

837

838 **Figure 6. (A) and (B)** C and O isotope compositions, and carbonate contents of the rock-suite
839 from La Pesca.

840

841 **Figure 7.** Sketch showing the reconstructed sequence of mineral reactions taking place in the
842 studied rock sequence. **1:** red garnet marble with eclogite pods (dark grey; **Fig. 2A**). **2:**
843 dolomite (and green garnet) marble layers from the hybrid rock domain. The grey bodies
844 represent the porphyroclastic dolomite replaced by diopside (e.g., **Fig. 3C**). **3:** pure antigorite
845 serpentinite with high-*P* metamorphic olivine veins (brown stripes). **4:** high-*P* hybrid
846 serpentinite (high-*P* ophicarbonate). The white bodies represent the neoblastic untwinned
847 dolomite that overgrows the silicate high-*P* phases in the serpentinite. Blue arrows: initial
848 release of H₂O fluid by serpentinite; orange arrow: CO₂ release from marbles due to dolomite
849 overgrowth by diopside; black arrows: COH fluid refluxing and carbonation of the high-*P*
850 serpentinite.

851

852 **Figure 8.** Pseudosection showing *P-T* estimates for **(A)** the high-*P* recrystallization of pure
853 serpentinite and **(B)** the high-*P* ophicarbonate. **(C)** represents a X_{H2O}-X_{CO2} pseudosection
854 showing the stable mineral assemblages and multivariant phase fields calculated for the high-
855 *P* ophicarbonate at fixed *P-T* conditions (*P* = 2 GPa and *T* = 550 °C, as indicated by the red star
856 in **Fig. 8B**). Modal amounts of olivine and clinopyroxene are also indicated by dotted blue and

857 solid grey lines, respectively.

858

859 **Figure 9.** General model for C recycling and carbonation of slab and forearc serpentinite.

Figure 1

- Late and post-orogenic deposits (Tertiary Piedmontese Basin)
- Sestri-Voltaggio Zone
- Erro-Tobbio metaperidotite
- Voltri metasediment + metabasalt
- Voltri serpentinites + eclogite
- Briançonnais continental basement

Garnet-dolomite marble + eclogite

Hybrid rocks serpentinite + marble

Serpentinite

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1

Table 1. Carbon and oxygen isotope compositions of rocks from La Pesca.

Sample	Description	Long	Lat	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	wt% carbonate
LP13-01	Pure serpentinite	E8.44645	N44.55311	- 9.1	22.2	0.37
LP13-02	Pure serpentinite	E8.44646	N44.55305	- 4.5	22.0	0.27
LP13-03	Carbonate vein in serpentinite	E8.44643	N44.55321	- 0.3	12.8	46.95
LP13-03V	Carbonate vein in serpentinite			1.8	23.0	12.66
LP13-04	Carbonate vein in serpentinite	E8.44638	N44.55366	0.2	13.8	72.25
LP13-05	Carbonate vein	E8.44639	N44.55369	0.7	11.9	16.77
LP13-06A	Serpentinite-vein contact	E8.44605	N44.55409	0.6	11.5	46.92
LP13-06V	Carbonate vein in serpentinite			0.5	13.5	100.18
LP13-07	Serpentinite-vein contact	E8.44636	N44.55387	- 2.3	22.2	1.07
LP13-10A	Finegrained red-garnet marble	E8.44623	N44.55402	1.8	13.5	57.88
LP13-10B	Finegrained red-garnet marble			1.3	13.9	18.74
<i>Transect across the hybrid zone</i>						
LP13-08	Pure serpentinite			- 6.6	21.8	0.06
LP13-09	Carbonate-bearing hybrid serpentinite (HP-opphicarbonate)	E8.44627	N44.55395	- 0.4	13.6	10.74
LP13-MA	Marble with green garnet			1.4	16.4	87.88
LP13-MB	Marble with green garnet			1.9	16.3	89.60
LP13-11A	Diopside-bearing dolomite marble	E8.44616	N44.55401	1.4	11.5	59.34
LP13-11B	Carbonate-bearing hybrid serpentinite (HP-opphicarbonate)			0.8	14.9	27.62
LP13-12	Carbonate-bearing hybrid serpentinite (HP-opphicarbonate)			1.6	12.7	16.21
LP13-13A	Marble with green garnet			0.6	15.2	42.32
LP13-13B	Marble with green garnet			0.9	18.0	39.32

All samples reacted for all carbonates (cc, dol, ank, mag) for 6hr reaction time at 72 °C.