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1 **Carbonation by fluid-rock interactions at High-Pressure conditions: implications for**
2 **carbon cycling in subduction zones**

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39 **Abstract**

40 Carbonate-bearing lithologies are the main carbon carrier into subduction zones. Their
41 evolution during metamorphism largely controls the fate of carbon, regulating its fluxes
42 between shallow and deep reservoirs. Recent estimates predict that almost all subducted
43 carbon is transferred into the crust and lithospheric mantle during subduction metamorphism
44 via decarbonation and dissolution reactions at high-pressure conditions. Here we report the
45 occurrence of eclogite-facies marbles associated with metasomatic systems in Alpine Corsica
46 (France). The occurrence of these marbles along major fluid-conduits as well as textural,
47 geochemical and isotopic data indicating fluid-mineral reactions are compelling evidence for
48 the precipitation of these carbonate-rich assemblages from carbonic fluids during
49 metamorphism. The discovery of metasomatic marbles brings new insights into the fate of
50 carbonic fluids formed in subducting slabs. We infer that rock carbonation can occur at high-
51 pressure conditions by either vein-injection or chemical replacement mechanisms. This
52 indicates that carbonic fluids produced by decarbonation reactions and carbonate dissolution
53 may not be directly transferred to the mantle wedge, but can interact with slab and mantle-
54 forming rocks. Rock-carbonation by fluid-rock interactions may have an important impact on
55 the residence time of carbon and oxygen in subduction zones and lithospheric mantle
56 reservoirs as well as carbonate isotopic signatures in subduction zones. Furthermore,
57 carbonation may modulate the emission of CO₂ at volcanic arcs over geological time scales.

58

59 **Keywords:** Subduction carbon cycle, Carbonation, CO₂ sequestration, Metasomatism

60

61 **1. Introduction**

62 Subduction exerts a key role in the long-term carbon cycle by regulating the fluxes of carbon
63 between the Earth's surface and the deep Earth. The redistribution of carbon between the
64 exogenic and endogenic reservoirs largely depends on the evolution of carbonate-bearing
65 lithologies in subduction zones. Carbonates are present in sedimentary, mafic and ultramafic
66 lithologies, and constitute the dominant reservoir of carbon in the subducting lithosphere (Alt
67 and Teagle, 1999; Kelemen & Manning, 2015). There is growing evidence that carbonates
68 can be extremely reactive during subduction metamorphism via devolatilization reactions
69 (Cook-Kollars et al., 2014; Kerrick & Connolly, 2001), as well as carbonate dissolution via
70 fluid-rock interactions at high-pressure conditions (Frezzotti et al., 2011; Ague and Nicolescu,
71 2014; Kelemen and Manning, 2015), carbonate reduction reactions (Galvez et al., 2013a;
72 Malvoisin et al., 2012), or melting of the subducting crust (Poli, 2015). Nonetheless, key
73 questions remain regarding the mechanisms of carbonic fluid transfer from the slab to the
74 lithospheric mantle in the sub-arc region, their role in mantle wedge metasomatism, and their
75 contribution to the CO₂ degassing at volcanic arcs.

76 To address these questions, a growing number of studies have been carried out using
77 both experimental petrology (Molina and Poli 2000; Poli et al., 2009) and thermodynamic
78 modeling (Kerrick and Connolly 2001; Gorman et al., 2006). All these studies agree that,
79 considering a "closed system" (no external fluid supply), significant carbon transfer to the
80 mantle wedge is feasible only at shallow depth in the forearc region. This transfer is made
81 possible via devolatilization reactions that, based on experimental and thermodynamic results,
82 are much more limited at deeper, subarc conditions (Connolly, 2005; Poli et al., 2009).
83 Nevertheless, the role of fluid-rock interactions appears to be critical for the stability of
84 carbonates. Recently, field based studies (Ague and Nicolescu, 2014; Frezzotti et al., 2011) as
85 well as theoretical and experimental works (Facq et al., 2014; Sverjensky et al., 2014) have
86 pointed out that massive carbonate dissolution in fluids may occur at high-pressure-low

87 temperature conditions and can generate large amounts of carbonic fluids (see Kelemen and
88 Manning, 2015 for review). Accounting for carbonate dissolution at high-pressure conditions
89 in comprehensive budgets overturns older paradigms on carbonate stability with respect to
90 carbon mobility in subduction zones. The most recent budgets actually predict that carbonate
91 dissolution allows almost all subducted carbon to be transferred to the mantle wedge
92 (Kelemen & Manning, 2015). Owing to the very recent discovery of these processes, much
93 remains to be learned about the fate of these carbonic fluids and their interaction with slab-
94 and mantle-forming rocks.

95 Here, we report the occurrence of eclogite-facies marbles formed by fluid-rock
96 interaction processes (metasomatism) occurring along intensely metasomatized lithological
97 interfaces (Alpine Corsica, France). We present and discuss the occurrence, textures,
98 mineralogy and geochemistry of these metasomatic marbles. We then propose a mechanism
99 of carbonates formation by precipitation and mineral carbonation by carbonic fluid-rock
100 interactions at high-pressure conditions. Finally, the implications and contribution of rock
101 carbonation to the deep carbon fluxes and cycling are discussed.

102

103 **2. Geological setting**

104 Alpine Corsica (France) is a branch of the Alpine orogenic system (Jolivet et al., 1991; Molli
105 and Malavieille, 2011) (Fig.1a). The belt mainly includes remnants of subducted Mesozoic
106 slow-spreading oceanic and passive margin lithosphere, which formed part of the Tethys
107 Ocean basin. This rock package is classically referred to as the Schistes Lustrés Complex
108 (Fig. 1b; Jolivet et al., 1990; Fournier et al., 1991; Malavieille et al., 1998; Vitale Brovarone
109 et al., 2013). The exceptional preservation of prograde-to-peak mineral assemblages,
110 including widespread lawsonite, makes the Schistes Lustrés of Alpine Corsica an excellent

111 site for field investigations related to subduction. These units underwent various metamorphic
112 overprints during the Alpine subduction ranging from subgreenschist-facies conditions of
113 about 300°C and 0.5 GPa to lawsonite blueschist and lawsonite eclogite-facies conditions
114 which reached 500-550 °C and ~2.3 GPa (e.g. Fournier et al., 1991; see Vitale Brovarone et
115 al., 2013 for review).

116 Carbonate-bearing rocks are widespread in the Schistes Lustrés of Alpine Corsica. The
117 most typical carbonate-bearing lithologies are metamorphosed oceanic sediments (referred to
118 as calcschists hereafter), ophicarbonates, and carbonated metabasalts (Miller et al., 2001;
119 Ravna et al., 2010; Vitale Brovarone et al., 2011b). In each lithology, primary carbonates and
120 various generations of carbonate veins are observed (Miller et al., 2001; Ravna et al., 2010;
121 Vitale Brovarone et al., 2011b). These veins have been shown to be in most cases in isotopic
122 equilibrium with the host rocks with little effect of external fluid infiltrations and
123 metasomatism (Cartwright and Buick, 2000). On the other hand, evidence for high-pressure-
124 low temperature fluid-rock interactions and metasomatism in the Schistes Lustrés of Alpine
125 Corsica is widespread, most typically localized at lithological interfaces. In this work, we
126 focus on processes occurring where serpentinites are in contact with metasedimentary rocks.

127 Here, past results on high-pressure metasomatism in Alpine Corsica are briefly
128 summarized. In the blueschist-facies zone, reactions between serpentinites and overlying
129 metasediments led to carbonate reduction and precipitation of wollastonite and abiotic
130 graphite at blueschist-facies conditions (Malvoisin et al., 2012; Galvez et al., 2013a). Except
131 for the influx of external, serpentinite-derived fluids, the reacted metasediments revealed
132 largely conservative carbon budget (Galvez et al., 2013a). In similar lithological settings,
133 massive precipitation of lawsonite from fluid-rock interactions at the expense of
134 metasedimentary rocks in contact with serpentinites testifies to the reincorporation of large
135 amounts of water in the rock at prograde blueschist-to-eclogite-facies metamorphic conditions

136 (Martin et al., 2011; Vitale Brovarone et al., 2014; Vitale Brovarone and Beyssac, 2014;).
137 This process is characterized by a dramatic whole-rock chemical modification leading to
138 mafic/ultramafic, Ca-rich metasomatic products.

139 The carbonate-rich rocks studied herein are intimately related to the latter Ca-rich
140 metasomatic rocks and were collected in the lawsonite eclogite-facies San Petrone unit. This
141 unit is characterized by a basal body of serpentinite variably overlain by Jurassic pillow
142 metabasalts, Mesozoic metasediments (e.g. calcschists, marbles, Mn-metacherts) or slivers of
143 Hercynian continental basement rocks mainly consisting of pre-Alpine, carbonate-free, high-
144 temperature metasediments and granitic rocks overprinted at high-pressure-low temperature
145 conditions during the Alpine subduction (Vitale Brovarone et al., 2011b; Fig. 1c).
146 Ophicarbonates are locally found at the top of the serpentinite body. The San Petrone
147 unit has been considered as a remnant of a Mesozoic hyper-extended passive margin (Vitale
148 Brovarone et al., 2011b; Beltrando et al., 2014). Peak metamorphic conditions in this unit are
149 estimated at ca. 490-530 °C and ~2.3 GPa by means of pseudosection modeling and
150 thermometry based on Raman spectroscopy of carbonaceous material (Ravna et al., 2010;
151 Vitale Brovarone et al., 2011a, 2013). The peak metamorphic age of ~34 Ma has been
152 determined by several techniques including U-Pb zircon and Lu-Hf garnet and lawsonite
153 geochronology (Martin et al., 2011; Vitale Brovarone and Herwartz, 2013).

154

155 **3. Structural occurrence of metasomatic marbles**

156 The carbonate-rich rocks which are the subject of this paper occur along a regional
157 lithological boundary separating serpentinites from either slivers of Hercynian basement
158 rocks (dominantly pre-Alpine high temperature metasedimentary rocks) or Mesozoic
159 metasedimentary rocks (Figs. 1c and 2). The first few meters of rock above the serpentinites

160 exhibit intense Alpine metasomatism that has already been described in previous studies
161 (Martin et al., 2011; Vitale Brovarone et al., 2011b, 2014). These metasomatic rinds can be
162 followed for several kilometers along the top of the serpentinite body and are characterized by
163 lawsonite-rich assemblages, but diopside-rich rocks are also common. These rocks are
164 referred to as Stage#1 diopside-lawsonite rocks (Fig.2). The carbonated rocks which are the
165 subject of this study are referred to as Stage#2 metasomatic marbles (or simply metasomatic
166 marbles), these form discontinuous patches or lenses of variable thickness and lateral
167 extension (from a few tens of cm to several m, Fig. 2), and are preferentially associated with
168 diopside-rich rather than the lawsonite-rich metasomatic rocks. The petrological differences
169 between Stage#2 metasomatic marbles and Mesozoic metasediments are discussed in Section
170 5.

171 The metasomatic marbles show a range of structural relationships with the surrounding
172 diopside-lawsonite rocks, and the carbonate/host rock ratios are extremely variable. Figure 2
173 summarizes the field relationships between the different rock types, i.e. serpentinites, Stage#1
174 diopside-lawsonite rocks, Stage#2 metasomatic marbles, and the inferred protolith rocks
175 (continental basement rocks or Mesozoic metasediments). The transition from diopside-
176 lawsonite rocks to Stage#2 metasomatic marbles is marked by a gradual increase of
177 carbonate/host rock ratio, passing from diopside-lawsonite rocks to isolated carbonate-rich
178 veins in Stage#1 host rocks, to Stage#2 metasomatic marbles with remnants of Stage#1 rocks.
179 Isolated veins have crack-seal texture and are mainly composed of rod-shaped Ca-carbonate \pm
180 omphacite (Figs. 3a, b, d). Carbonate rods are perpendicular to the vein walls (Fig. 3b).
181 Omphacite grows from the vein wall toward the center (Fig. 3d). Some veins exhibit
182 interaction with the host Stage#1 rocks characterized by omphacite replacement of the
183 precursor diopside (Al-Na gain; Ca-Mg loss) and local carbonate precipitation (Fig. 3d). The
184 abundance of omphacite decreases from the vein wall to the host rock. Diopside far from the

185 vein does not display any chemical zoning involving Na-Al enrichment. The isolated veins
186 are connected to dm-thick layers (ca. 20 cm) showing similar crack-seal textures (Figs. 2 and
187 3a). These layers are meter-scale and are parallel to the wallrock foliation (Fig. 2). Outcrop-
188 scale hydraulic breccias consisting of cm- to m-scale angular clasts of Stage#1 diopside-
189 lawsonite rocks embedded within a carbonate vein network provide strong evidence for
190 diffuse hydrofracturing and carbonate precipitation (Figs. 2, 3e and f).

191 In some outcrops, serpentinites are overlain by a sequence of metasomatic marbles ranging in
192 thickness from less than one m to ~10m (Figs. 2, 3g and 4a). These metasomatic marbles are
193 hosted within the diopside-lawsonite rock and contain remnants of the host rock—ranging
194 from a few microns to several centimeters—floating in a carbonate-dominated matrix.
195 Remnants of diopside-lawsonite rocks in the metasomatic marbles differ from the angular
196 clasts found in the hydraulic breccias. First, they have embayed margins and microtextures
197 (see Section 5) suggest digestion of the silicate portions into the carbonate matrix. Second, the
198 host rock remnants preserve their original orientation (Fig. 4a), whereas the clasts in the
199 hydraulic breccias have random rotation (Figs. 2). Last, the diopside remnants are commonly
200 rimmed by omphacite, the latter being in textural equilibrium with the carbonate as observed
201 in the isolated carbonate veins.

202

203 **4. Methods**

204 *4.1 Scanning electron microscopy and electron microprobe*

205 Petrographic thin sections were carbon coated for scanning electron microscopy (SEM).
206 Observations were performed at a working distance of 7.5 mm using a Zeiss Ultra 55 field
207 emission gun SEM operated at 15 kV with a 120 μm aperture. Backscattered electron (BSE)
208 mode was used to investigate chemical heterogeneities using an Angle Selective

209 Backscattered Detector (AsB) or an Energy Selective Backscattered Detector (EsB). Energy
210 dispersive X-ray spectrometry (EDXS) maps were acquired using an EDXS QUANTAX
211 system equipped with a silicon drift detector XFlash 4010 (Bruker). Data were processed with
212 the software Esprit (Bruker). Mineral analyses were performed on a Cameca electron
213 microprobe (either SX-100 or SX Five) (Camparis, Université Paris 6). Common analytical
214 conditions were adopted for spot analyses [15 kV, 10 nA, wavelength-dispersive spectroscopy
215 (WDS) mode], using Fe₂O₃, MnTiO₃ (Mn, Ti), diopside (Mg, Si), orthoclase (Al, K),
216 anorthite (Ca) and albite (Na) as standards. The automated Cameca ZAF procedure was used
217 for quantification (Tables S1, S2, S4 and S5).

218 *4.2 Whole rock major and trace element data*

219 Chips of low to highly carbonated rock were removed from hand-samples. Samples were
220 crushed in an agate mortar (grain size < 80µm) and sent for major and trace element, CO₂ and
221 organic carbon analyses at the Service d'Analyse des Roches et Minéraux (SARM, Centre de
222 Recherches Pétrographiques et Géochimiques, Nancy, France) by alkali fusion of rock
223 samples (LiBO₂), followed by concentration measurements using an ICP-OES Icap 6500
224 (Thermoscientific) for major elements, and an ICP-MS X7 (Thermoscientific) for minor
225 elements (protocol by Carignan et al., 2001). The modal proportions of silicates vs. carbonate
226 were estimated first with optical microscopy and then checked using whole rock and mineral
227 composition. In two cases, samples 1COR12-20d and COR13-29c, two different chips were
228 taken: one representative of the metasomatic marble, where silicates are present as clasts, and
229 another one representative of a Stage#1 diopside+lawsonite rock, where carbonate is a minor
230 constituent. When an average value is indicated, the standard deviation (1σ) is also reported
231 (Tables 1 and S2).

232 *4.3 Carbon mass balance calculation*

233 In/out carbon fluxes in the subducting slab (during high-pressure metamorphism) are
234 estimated from the grams of CO₂ per 100g of rock released by decarbonation reaction and
235 carbonate dissolution vs. the grams of CO₂ per 100g of rock bound by rock carbonation
236 process (Section 8.3). The CO₂ bound in the rocks of this study was back calculated from
237 whole rock analyses removing the measured organic carbon content to the measured CO₂ (red
238 bar in Fig. 8a, see also Table S2). Values for CO₂ released per 100g of rock after carbonate
239 dissolution (Ague and Nicolescu, 2014) and decarbonation of calcschists (Cook-Kollars et al.,
240 2014) are taken from the literature. For the data on carbonate dissolution (Ague and
241 Nicolescu, 2014), we took the average of the estimated CO₂ loss in samples from Syros
242 (35.1g) and Tinos (22.2g), thus resulting in 28.65 g of CO₂ lost during carbonate dissolution
243 (blue bar in Fig. 8a). For samples affected by decarbonation, we took the calcschist modeled
244 by Cook-Kollars et al. (2014). This rock initially contains 40 wt.% carbonate (i.e. the initial
245 CO₂ content is 17.6g per 100 of rock) and it loses 50% of its initial CO₂, thus 8.8g per 100g of
246 rock (green bar in Fig. 8a). Cook-Kollars et al. (2014) highlighted that natural samples from
247 Schist Lustrés and Cignana suite show a lower extent of decarbonation. They conclude that
248 decarbonation reactions during metamorphism may cause the loss of 10 to 20% of the initial
249 CO₂. We took the intermediate value of 15%. Thus, considering the same initial CO₂ content
250 of 17.6g per 100 g of precursor rock, the CO₂ lost is 2.64g per 100g of rock (orange bar in
251 Fig. 8a).

252 *4.4 Stable isotope data*

253 *4.4.1 Carbon and Oxygen isotopes of calcite*

254 Chips of carbonate were taken from hand-samples and crushed in an agate mortar. Raman and
255 SEM analyses establish that the carbonate is nearly pure Ca-carbonate. The isotopic
256 composition of calcite was measured by an AP2003 continuous flow mass spectrometer at

257 LGIS, IPGP. Approximately 2 to 2.5 mg of sample were loaded in vials; three standards of
258 pure calcite were also used for calibration of both concentration and isotopic composition.
259 After flushing with ultrapure helium, orthophosphoric acid (H_3PO_4) was introduced in each
260 tube in order to produce gaseous CO_2 . After 4 hours of reaction at ambient temperature,
261 calcite completely decomposes to release CO_2 (McCrea, 1950); gases were then transferred
262 into the mass spectrometer for analysis. In order to improve the precision of the
263 measurements, each analysis was repeated four times for each vial, and each sample analysed
264 twice. The isotopic $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios are expressed using the conventional δ -notation
265 relative to PDB and SMOW international standards. The precision is 0.1‰ for $\delta^{13}\text{C}$ and 0.2‰
266 for $\delta^{18}\text{O}$. The results are reported in Table S3. When an average value is indicated, the
267 standard deviation (1σ) is also reported.

268 4.4.2 Oxygen isotopes of clinopyroxene

269 A polished sample of omphacite+carbonate vein hosted in diopside-lawsonite rock was first
270 studied by SEM to identify zones representative of Stage#1 diopside and Stage#2 omphacite
271 (Figs. 3d and S2). Aliquots of carbonate+omphacite vein were crushed ($<100\ \mu\text{m}$) and single
272 crystals of omphacite were separated by handpicking under a binocular microscope. Diopside-
273 rich protolith rock was sampled out of the vein selvage (ca. 2 cm from the vein) in order to
274 avoid the isotopic contribution of the vein-related omphacite rims, as checked by SEM. Rock
275 was crushed ($<100\ \mu\text{m}$) and single crystals of diopside were separated by handpicking under a
276 binocular microscope. Approximately 2 mg of omphacite and 2 mg of diopside were analyzed
277 using laser fluorination at IPGP (Paris, France) along with UWG-2 garnet standard.
278 Analytical methods are similar to those documented in Rumble et al. (1997). The oxygen
279 isotopic ratios are reported using the international V-SMOW standard. Measurement of
280 UWG-2 garnet standard aliquots gave 2σ external error on $\delta^{18}\text{O}$ of $\pm 0.036\text{‰}$, which is in the

281 same range of in-run uncertainties for individual measurements (<0.03‰). Measurements
282 were duplicated for omphacite, while for diopside the material collected was not sufficient.
283 Fractionation factors (Hoffbauer et al., 1994) were used to infer oxygen isotopes equilibrium
284 temperature between carbonate and clinopyroxenes (Table S3.1). Estimated errors using a
285 Monte Carlo simulation on the calculated temperatures are 30°C and 20°C for the omphacite-
286 calcite and diopside-calcite equilibrium, respectively.

287

288 **5. Petrography of selected metasomatic marbles**

289 Metasomatic marbles have characteristic features that make them different from any other
290 carbonate-bearing rocks of the Schistes Lustrés (i.e. Mesozoic impure marbles, calcschists
291 and ophicarbonates), although they may display mineralogical and chemical variations from
292 one to another outcrop. As an example, the matrix carbonate in these rocks systematically
293 displays a rod-shaped habit with rods oriented at high angles to the regional schistosity or to
294 the margin of Stage#1 clasts in hydraulic breccias (Fig. 3b). In all but one metasomatic
295 marble, the carbonate is a Ca-carbonate phase. Matrix carbonate is calcite, whereas aragonite
296 was found as inclusions in garnet and apatite (see Fig. S1). Dolomite was detected in only one
297 sample by Raman spectroscopy and it was in very small proportions compared to Ca-
298 carbonate (dolomite content below X-ray diffraction detection limit). No ankerite was
299 observed in these rocks, whereas it is common in calcschists and ophicarbonates of the
300 Schistes Lustrés. As Ca-carbonate is the dominant carbonate phase, we will use hereafter the
301 term "carbonate" to indicate compositionally pure Ca-carbonate (i.e. calcite after aragonite).

302 In thin section, metasomatic marbles display a characteristic structure defined by carbonate-
303 rich and diopside-lawsonite-rich domains, the latter occurring as either continuous layers or
304 isolated patches (Figs. 4b, d, e). A compositional layering is defined by the alternation of

305 carbonate aggregates with diopside (\pm lawsonite) aggregates. Calcite rods are mm-sized;
306 diopside and lawsonite grain size ranges from μm to mm. The mineral assemblage most
307 commonly consists of carbonate, diopside and lawsonite, with modal proportions varying
308 from sample to sample (Fig. 4). Garnet is also present in several samples. It is found as
309 euhedral, μm to mm-sized crystals in textural equilibrium with carbonate. Its composition
310 ranges from grossular to almandine-spessartine solid solution (Table S4). Phengite, epidote,
311 quartz and pumpellyite (Table S5) are also present. Common accessory phases are titanite,
312 apatite and graphite. Although such assemblages are described in calcschists in the Western
313 Alps (see e.g. Cook-Kollars et al., 2014), they have never been documented in Alpine Corsica
314 to our knowledge. Moreover, the textural and mineralogical features of these silicates indicate
315 that they resulted from intense metasomatism during their high-pressure evolution, as
316 described below.

317 For simplicity, two dominant mineralogical assemblages representative of Stage#1 and
318 Stage#2 rocks are distinguished, i.e. diopside + lawsonite and carbonate + omphacite,
319 respectively. As mentioned above, additional phases may be present from one sample to
320 another. The chronological relations between the two mineralogical assemblages may be
321 deciphered from the outcrop-scale down to the micro-scale. Diopside (Quadrilateral_{96,5}
322 Aegirine_{3,5}; classification after Morimoto, 1989; see Tab. S1) formation at high-pressure
323 conditions during subduction is demonstrated by: (i) the occurrence of diopside veins cross-
324 cutting lawsonite-bearing fabrics (Fig. 3d) and (ii) the fact that the diopside veins are in turn
325 cut by carbonate+omphacite veins, indicating near peak P-T metamorphic conditions. In the
326 carbonate-bearing domains, diopside in contact with carbonate shows either embayed grain
327 boundaries or newly-formed compositional coronas of omphacite (Figs. 5a; Jadeite_{39,5}
328 Quadrilateral_{44,5} Aegirine₁₆; see Tab. S1). Tiny (c.a. 10-20 μm), second generation idioblastic
329 lawsonite crystals were locally found in the carbonate. In the vein selvage, omphacite rims on

330 diopside (Fig. 5b) have the same composition as omphacite growing together with carbonate
331 in the vein. In metasomatic marbles, atoll-like textures show relict diopside cores being
332 replaced by carbonate and rimmed by omphacite (Fig. 5a), the latter being in textural
333 equilibrium with the carbonate matrix. The abundance of omphacite varies from one sample
334 to another. All transitional stages from carbonate-free diopside-lawsonite rocks to carbonate-
335 rich rocks are depicted in Figure 4.

336 Only one sample (COR13-21d) displays a different mineralogy, composed of (in order of
337 volume abundance): calcite, actinolite, chlorite and clinopyroxene. This sample was collected
338 within a sequence of typical metasomatic marbles, and shares with them similar characteristic
339 features such as rod-shaped carbonate and Na-rich clinopyroxene coronas (aegirine-augite,
340 Na-Fe³⁺ rich clinopyroxene, see Fig. 5c) on relict diopside. Geochemical data for this sample
341 are given in Section 6.

342

343 **6. Whole rock chemical compositions**

344 Samples of metasomatic marbles were analyzed for their major and trace element bulk
345 composition (Table S2). Reference samples of Mesozoic calcschist and ophicarbonates
346 unaffected by metasomatism (i.e. far from the studied lithological boundaries and showing no
347 mineralogical or textural evidence for fluid-rock interactions), were also analyzed (Table S2).
348 Table 1 reports the average major element composition of metasomatic marble as well as the
349 compositions of a Stage#1 diopside-lawsonite rock (sample OF3598 in Vitale Brovarone et
350 al., 2014) and a Stage#1 rock with higher lawsonite content (lawsonite mode c.a. 75%;
351 sample COE5, Martin et al., 2011).

352 The variability of both Stage#1 rocks and Stage#2 metasomatic marbles hampers
353 quantitative mass balance calculation. Here, only concentrations of the most representative

354 oxides CaO, MgO, SiO₂ and CO₂ are presented. Metasomatic marbles have variable
355 compositions based on the carbonate-silicate modal proportions (Tables 1, S2). The average
356 composition is: CaO 39 wt.% ($\pm 5\%$, 1σ); CO₂ 27 wt.% ($\pm 6\%$, 1σ); SiO₂ 20 wt.% ($\pm 6\%$, 1σ)
357 and MgO 3 wt.% ($\pm 2\%$, 1σ). The silicate mode in sample COR13-21d is higher, thus
358 resulting in a slightly different bulk rock composition (CaO 22%; CO₂ 12%; SiO₂ 37%). Even
359 accounting for the lower carbonate content, sample Cor13-21d has an Mg-rich composition
360 (MgO 11 wt.%) compared to metasomatic marbles.

361 Comparing the average composition of metasomatic marbles with Stage#1 diopside-
362 lawsonite rock (Table 1), the following features can be outlined. Despite the variability of the
363 protolith (with more or less abundant lawsonite), CaO is always enriched (CaO in
364 metasomatic marbles is about double that in Stage#1 rocks). MgO variations are more
365 difficult to evaluate, as they depend not only on the silicate content of metasomatic marbles,
366 but also on the initial diopside modal proportion of Stage#1 rock (cf. samples OF3598 and
367 COE5, Table 1). The reference calcschist (sample COR13-32) fits the range of compositions
368 of Alpine calcschists (Busigny et al. 2003, Galvez et al., 2013b). The reference ophicarbonated
369 sample (sample COR13-30a), has a Mg-rich composition (13 wt.% vs. 3 wt.% in metasomatic
370 marbles), similar to sample COR13-21d.

371 Whole-rock Rare-Earth Element (REE) analyses of most analyzed samples have
372 positive slopes ($La_N/Lu_N > 1$) comparable to the reference calcschist and the host diopside-
373 lawsonite rock formed at the expense of carbonate free, continental basement
374 metasedimentary rocks (Fig. 6; Martin et al., 2011; Vitale Brovarone et al., 2014). Only
375 sample COR13-21d differs significantly. It has a rather flat REE pattern, except for a slight
376 negative Ce anomaly (Fig. 6). This pattern matches reasonably well with the ophicarbonated
377 standard and passive margin serpentinites (Barnes et al., 2014; Deschamps et al., 2013;
378 Kodolányi et al., 2011). This sample also has a significantly higher Ni and Cr content than the

379 other analyzed samples (1022 and 2114 ppm respectively, Table S2). These patterns suggest
380 an ultramafic signature for this sample.

381

382 **7. Carbon and oxygen stable isotope analysis of Ca-carbonate and clinopyroxene**

383 C and O isotopic compositions of calcite from metasomatic marbles (including veins) were
384 analyzes, as well as the O isotopic compositions of Stage#1 diopside and Stage#2 omphacite.
385 For reference, calcite from calcschist and ophicarbonates was also analyzed. Analyses of
386 carbon and oxygen isotopes of calcite are reported in Table S3.

387 For all samples (reference calcschists and ophicarbonates as well as metasomatic
388 marbles) calcite $\delta^{13}\text{C}$ values vary little and average 1.1‰ (± 1.2 , 1σ) (Fig. 7a), consistent with
389 marine sedimentary carbonate rocks (Plank and Langmuir, 1998). The average calcite $\delta^{18}\text{O}$
390 value of metasomatic marbles is 14.3‰ (± 3.2 , 1σ) (Fig. 7a). The two reference calcschists
391 (from ca. 8 to 50 m from the serpentinite, across strike) have an average $\delta^{18}\text{O}$ of 21.5‰ (± 1.5 ,
392 1σ). The ophicarbonates analyzed in this study have $\delta^{18}\text{O}$ of 11‰. Carbonate in veins cutting
393 across carbonate-free, diopside-rich rocks has very low $\delta^{18}\text{O}$ 10.6‰ (± 0.2 , 1σ), independent
394 of vein distance from the serpentinite. Carbonate in samples collected from outcrops with
395 higher carbonate/silicate ratios (e.g. carbonate mode 70%) display more dispersed values that
396 vary from ~12 to ~18‰. In these rocks, samples collected a few centimeters from the
397 serpentinite body have an average value of ~14‰ (9 samples), whereas the two samples
398 collected far from the serpentinite (i.e. more than 3m) and within the analyzed interaction
399 zone (cf. Figs. 6 and S3 and Table S3 for sample location and respective REE patterns and
400 isotope composition) have a heavier signature of ~18‰. A simple correlation cannot be
401 established between the distance from the serpentinite and the $\delta^{18}\text{O}$ values within the reaction
402 zone. Indeed, Stage#2 omphacite-carbonate veins far from the serpentinite body (up to 8 m

403 from the contact) have low $\delta^{18}\text{O}$ values similar to metasomatic marble sampled a few cm from
404 the serpentinite body (e.g. samples 2COR14-4i and 1COR14-11a; Table S3). However, taken
405 as a whole, metasomatic marbles, overlying the serpentinite body, have lower $\delta^{18}\text{O}$ compared
406 to the reference calcschists. Indeed, calcschists that lack the petrographic characteristics of
407 intense fluid-rock interaction present in metasomatic marbles always have heavier values (ca.
408 21‰, see samples COR13-32 and 1COR12-11Q, Table S3), even if they crop out at less than
409 1m from the metasomatic zones.

410 Reconnaissance oxygen isotope measurements on silicate minerals were performed in
411 order to test for isotopic equilibrium between the two clinopyroxene generations (Stage#1
412 diopside and Stage#2 omphacite) and the vein infill carbonate. The analyzed sample is
413 composed of the host Stage#1 diopside-rich rock cut across by a Stage#2 calcite-omphacite
414 vein (Figs. 3d and S2). Diopside has $\delta^{18}\text{O}$ values of $\sim 6\text{‰}$. Vein infill omphacite has heavier
415 $\delta^{18}\text{O}$ of $\sim 7\text{‰}$. Fractionation factors available from literature data ($\Delta_{\text{calcite-clinopyroxene}}$ from
416 Hoffbauer et al., 1994, , Table S3.1), give equilibrium temperature of 494°C ($\pm 30^\circ$) for the
417 omphacite-carbonate assemblage and 426°C ($\pm 20^\circ$) for diopside-carbonate using the same
418 database. These differing temperatures are consistent with textural disequilibrium between the
419 mineral pairs (carbonate-diopside and diopside-omphacite). The omphacite-calcite
420 thermometer yields temperatures closer to the estimated peak T conditions of the
421 metamorphic unit ($490\text{-}530^\circ\text{C}$, see Section 2). This observation suggests isotopic equilibrium
422 for the omphacite+carbonate paragenesis and confirms the microtextural observations (see
423 Section 5).

424 Equilibrium was likely reached by fluid-mediated reactions. However, this
425 interpretation must be taken with caution because only one sample was analyzed. The
426 composition of an aqueous fluid in equilibrium with these minerals was also calculated at 500
427 $^\circ\text{C}$ (i.e. near peak conditions). The $\delta^{18}\text{O}$ of a fluid in equilibrium with the measured Ca-

428 carbonate is 10.1‰ ($\Delta_{\text{cal-H}_2\text{O}}=0.62$, Zheng et al. 1994). For the analyzed omphacite
429 composition, the water $\delta^{18}\text{O}$ obtained is 8.4‰ ($\Delta_{\text{di-H}_2\text{O}}=-1.95$, $\Delta_{\text{ae-H}_2\text{O}}=-0.07$ and $\Delta_{\text{jd-H}_2\text{O}}=-0.14$,
430 Zheng et al., 1993). Although the fractionation factors for lawsonite are not available, the
431 diopside-water equilibrium, can be used as a proxy for fluid in equilibrium with the Stage#1
432 assemblage implying that the fluid $\delta^{18}\text{O}=8\text{‰}$. The mismatch between calcite-water and
433 omphacite-water oxygen composition equilibrium is quite small as well as for water in
434 equilibrium with diopside. It is worth noting that the estimated fluid composition is similar for
435 both metasomatic stages.

436

437 **8. DISCUSSION**

438 *8.1 Fluid-mediated carbonation at high-pressure conditions*

439 Detecting metasomatism in metasedimentary rocks is often challenging owing to the
440 variability of protolith compositions (Bebout and Burton, 1989; Ague, 2003). The occurrence
441 of carbonate in metasedimentary rock is common, and in most cases likely reflects the
442 primary composition of the subducted rocks. However, the direct spatial association of
443 Stage#2 metasomatic marbles along major fluid conduits characterized by intense
444 metasomatism (Martin et al., 2011; Vitale Brovarone et al., 2014) suggests that the evolution
445 of these rocks was mediated by the interaction with external fluids (e.g. Ague, 2003).

446 Rod-shaped calcite crystals in marbles from eclogite-facies terrains have been
447 described in Syros (Greece) and the Sivrihisar belt (Turkey) (Brady et al., 2004; Seaton et al.,
448 2009), and have been interpreted as topotactic pseudomorphs of calcite after aragonite. Both
449 studies regard carbonate as a primary constituent of the rock and do not consider fluid-
450 mediated precipitation. In the study case, we consider this hypothesis unlikely based on

451 several lines of evidence. Textures like crack-seal and networked carbonate veins cutting
452 across carbonate-free metasomatic rocks suggest high pore fluid pressure and hydrofracturing
453 (e.g. Bebout and Barton, 1989). This evidence clearly points to the percolation of carbonic
454 fluids along lithological boundaries, and their precipitation of carbonate. As reported in
455 Sections 2 and 5, field relations and microstructural features (Figs. 4) suggest carbonation of
456 the Ca-Mg-rich silicate rocks. The lateral (along schistosity) transition from carbonate-free
457 diopside-lawsonite rocks and metasomatic marbles is evidence for chemical interaction
458 occurring between a carbonic fluid and the host-rock assemblage. Progressive replacement of
459 diopside-rich rocks by carbonate is demonstrated at the microscale by the corroded texture of
460 precursor minerals (embayed and atoll-like diopside, Figs. 4d, e and 5a) and producing
461 coronas in contact with carbonates (e.g. omphacite rims on diopside, Figs. 5a and b). The
462 carbonate isotopic composition presented in this work (Section 7) further supports the
463 hypothesis of fluid-mediated carbonate precipitation. All metasomatic marbles are composed
464 of Ca-carbonate (calcite after aragonite). This appears unlikely in the case of metamorphic
465 recrystallization of rocks containing significant whole rock Mg (Table S2). These
466 observations suggest that carbonate precipitation occurred via two concurrent processes of
467 fluid-rock interaction: crack-sealing (carbonation by volume increase, Section 3) and mineral
468 replacement (Section 5). Note that carbonation of mafic rocks during high-pressure
469 metamorphism was also suggested by Boundy et al. (2002) for eclogite-facies rocks from the
470 Lindås Nappe (Caledonides, Western Norway) and by Kleine et al. (2014) for blueschist-
471 facies rocks from Syros. Both authors proposed carbonation of mafic eclogites along a shear
472 zone affected by fluid circulation. Similarly, Nishiyama (1990) proposed metamorphic
473 carbonation during exhumation of blueschist-facies metabasic rocks in association with
474 serpentinites in the Nishisonogi metamorphic complex (Japan).

475 Based on these observations, the metasomatic history of the Corsican eclogite-facies marbles
476 can be subdivided into two stages, both occurring at high-pressure conditions during
477 subduction.

478 *Stage#1*: calcic metasomatism of protolith metasedimentary rocks or continental basement
479 transforms metasediments in contact with serpentinites to Ca-Mg rocks dominantly composed
480 of diopside and lawsonite during prograde metamorphism (cf. Martin et al., 2011; Vitale
481 Brovarone et al., 2014).

482 *Stage#2*: carbon-bearing fluid reacts with the pre-existing diopside-lawsonite rock and
483 associated serpentinites leading to the precipitation of carbonate-dominated assemblages as
484 either crack-filling material, or by replacing silicate minerals. The metamorphic conditions for
485 this stage are constrained to high-pressure conditions by the assemblage aragonite +
486 omphacite + lawsonite + garnet that characterize several of the analyzed samples ($P > 1.5$
487 GPa at 450-500 °C), and supported by the estimated O isotope Ca-carbonate-omphacite
488 equilibrium T of ca. 500 °C.

489 *8.2 Stable isotopes: marker of rock carbonation and fluid source?*

490 Stable isotope geochemistry has provided important information for the study of high-
491 pressure metasomatic processes involving carbonates (Valley 1986; Wang & Rumble 1999;
492 Ague and Nicolescu, 2014; Galvez et al., 2013a,b). The trends of decreasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$
493 isotopic composition of the metamorphic carbonates may be attributed to: (i) inheritance of
494 protolith isotopic signatures (Wang and Rumble, 1999), (ii) carbonate-silicate isotopic
495 exchange; (iii) devolatilization reactions driven by increasing temperatures (Wang and
496 Rumble, 1999), or (iv) interaction with COH fluids (Ague and Nicolescu, 2014; Galvez et al.,
497 2013a,b).

498 In this study, hypothesis (i) can be ruled out by comparison of the isotopic signature of
499 metasomatic marbles with calcschists far from the metasomatic zones. The reference
500 calcschists have $\delta^{13}\text{C}$ values of ca. 0‰ and $\delta^{18}\text{O}$ of ca. 21‰ similar to those of calcschists and
501 carbonate veins (for similar metamorphic conditions) in Alpine Corsica (Cartwright and
502 Buick, 2000; Miller et al., 2001), Western Alps (Cartwright and Barnicoat, 1999; Cook-
503 Kollars et al., 2014), and Cyclades (Ague and Nicolescu, 2014) (Fig. 7a). The metasomatic
504 marble $\delta^{13}\text{C}$ values are shifted toward heavier values, although still overlapping the
505 compositional range of seawater carbonates, whereas $\delta^{18}\text{O}$ values display a much greater
506 dispersion towards lower values (Fig. 7a).

507 Partial silicate-carbonate oxygen isotope exchange (hypothesis ii) is an alternative way
508 to explain low $\delta^{18}\text{O}$ (with almost no change in $\delta^{13}\text{C}$). We discard this scenario for two
509 reasons. 1) At temperatures of 500°C, isotopic exchange by diffusion between two solid
510 phases is expected to be very slow and thus restricted to grain margins. 2) Even if interface-
511 coupled dissolution precipitation allowed faster isotopic exchange (Putnis and John, 2010),
512 the $\delta^{18}\text{O}$ achieved in the carbonate after such equilibration should be correlated with the
513 silicate content (the lowest $\delta^{18}\text{O}$ being observed for the highest silicate content; Wang and
514 Rumble 1999; Cook-Kollars et al. 2014). Figure 7b shows that no correlation exists between
515 the $\delta^{18}\text{O}$ of carbonate and the silicate content in the rock.

516 As a test for the third hypothesis, the metasomatic marbles are compared with
517 carbonates that have experienced devolatilization reactions. Carbonates in skarns formed by
518 contact metamorphism are characterized by a strong decrease of $\delta^{13}\text{C}$ coupled with a smaller
519 $\delta^{18}\text{O}$ decrease during decarbonation (e.g. Valley 1986). The trend observed in Corsican
520 metasomatic marbles of $\delta^{18}\text{O}$ decreasing with $\delta^{13}\text{C}$ remaining constant is actually different
521 from a devolatilization trend (Fig. 7c).

522 Considering the compelling evidences for fluid-rock interactions and metasomatism,
523 interactions between rocks and COH fluids (hypothesis iv) is considered the most likely
524 hypothesis. Galvez et al. (2013b) reported carbonate reduction to graphite in contact with
525 serpentinites in the high-pressure units of Alpine Corsica. In this study, carbonates display a
526 peculiar variation showing a decreasing $\delta^{18}\text{O}$ coupled with increasing $\delta^{13}\text{C}$. Residual
527 carbonate in samples affected by carbonate dissolution driven by serpentinite-derived fluids
528 described by Ague and Nicolescu (2014) show a drop in oxygen isotopic signature compared
529 to the protolith (6 to 10‰ lower values). However, changes in $\delta^{13}\text{C}$ are very small, with only
530 a 1.5‰ decrease. Both carbonate precipitation and dissolution seem to be characterized by a
531 large decrease in $\delta^{18}\text{O}$ and little to no change in $\delta^{13}\text{C}$ (Fig. 7c; cf. Section 8.3 for additional
532 discussion). The $\delta^{13}\text{C}$ values of metasomatic marbles are similar to those typical of carbonates
533 in marine sediments (e.g. Hoefs, 2013) and subducted oceanic suites ($\delta^{13}\text{C}$ close to 0‰; e.g.
534 Miller et al., 2001), thus indicating that carbon in the fluids derives from marine carbonates,
535 likely from the overlying carbonate-bearing metasedimentary rocks. The low $\delta^{18}\text{O}$ values
536 rather point to fluids equilibrated with silicates in mafic or ultramafic rocks, possibly
537 including Stage#1 metasomatic rocks (Miller et al., 2001; Martin et al., 2014; Vitale
538 Brovarone et al., 2014; Angiboust et al., 2014). The large serpentinite body in contact with
539 the rocks of this study would represent a plausible source for aqueous fluid with a light
540 oxygen signature. Despite the lack of evidence for serpentinite dehydration (e.g. metamorphic
541 olivine) in the samples from Alpine Corsica, a growing number of studies (Faccenda 2014;
542 Wilson et al., 2014) have proposed that fluids generated at depth can move up along the plate
543 interface and interact with shallower slab-forming rocks. Ague and Nicolescu (2014)
544 proposed that fluid equilibrated with mafic and ultramafic rocks can drive stoichiometric
545 carbonate dissolution, resulting in aqueous fluid enriched in carbon with $\delta^{13}\text{C}$ around 0‰.
546 However, if fluids were diluted, the contribution of oxygen from dissolved carbonates to the

547 oxygen isotopic signature of the fluid is expected to be very low. The preservation of
548 lawsonite requires very low X_{CO_2} fluid concentrations ($X_{\text{CO}_2} < 0.005$; e.g. Nitsh, 1972),
549 demonstrating that the carbon-bearing fluid was dominantly aqueous. Altogether, these
550 considerations point to metasomatic marbles formation by interaction with aqueous fluids
551 bringing isotopic signatures of both dissolved carbonates and mafic/ultramafic reservoirs.

552

553 *8.3 Rock carbonation during subduction: implications for the deep carbon cycle*

554 The behavior of carbonate, more specifically Ca-carbonate, during subduction has long been a
555 matter of debate. Few experimental studies of Ca-carbonate solubility in H_2O have been
556 conducted at P-T conditions appropriate for subduction metamorphism (Walther and Long,
557 1986; Fein and Walther, 1989; Newton and Manning, 2002; Caciagli and Manning, 2003;
558 Manning et al., 2013; Facq et al., 2014). Caciagli and Manning (2003) showed that calcite
559 solubility increases with P and T at high-pressure conditions. Ca-carbonate dissolution at
560 high-pressure conditions has been demonstrated to be very efficient in natural environments
561 ($P > \sim 2$ GPa, Frezzotti et al., 2011; Ague and Nicolescu, 2014), and it is now considered as a
562 major process for the mobilization of carbon in subduction zones (Kelemen & Manning,
563 2015). Carbonic fluids produced by carbonate dissolution are thus a potential source of
564 carbon for carbonate precipitation in subduction zones. Figure 8a shows a rough carbon
565 fluxes mass balance (see Section 4.3 for method of carbon fluxes calculation) considering
566 carbon bound by rock carbonation in metasomatic marbles vs. the amount of carbon dioxide
567 released by dissolution and devolatilization reactions estimated in previous field-based studies
568 in analog geological settings (Ague and Nicolescu, 2014; Cook-Kollars et al., 2014). The
569 amount of CO_2 released by decarbonation (green and orange bars) is small compared to that
570 released by dissolution (blue bar). Consequently, processes related to carbonate solubility

571 mobilize carbon in greater quantities than simple decarbonation reactions (Ague and
572 Nicolescu, 2014). A possible explanation for this result is that devolatilization reactions are
573 controlled and limited by the presence of silicate phases with which the carbonate minerals
574 can react, regardless of the fluid fluxes. The red bar in the diagram indicates the inferred
575 amount of CO₂ transferred from the fluid to the rock by rock carbonation, considering an
576 initial carbon content of 0 g per 100g of precursor rock. The amount of carbon bound per
577 100g of rock is directly comparable with that released by carbonate dissolution. This
578 observation suggests that a large amount of dissolved carbon can be re-bound into the solid
579 phase by rock carbonation, and that carbonate dissolution and rock carbonation at high-
580 pressure conditions are both crucial processes controlling carbon fluxes during subduction.

581 Slab-parallel ascent of fluids may represent a suitable configuration to enhance the efficiency
582 of rock-carbonation reactions, if favorable conditions occur (Lazar et al., 2014; Kelemen and
583 Manning, 2015; Sverjensky et al., 2014). Figure 8b shows the Ca-carbonate solubility in
584 aqueous fluid as a function of P and T (after Kelemen & Manning 2015) along with the
585 predicted P-T path for cold subduction (after Syracuse et al., 2010). Deep metamorphic fluids
586 ascending parallel to the downgoing slab would cut across the solubility curves during their
587 ascent. Although prediction of fluid slab-parallel ascent by numerical modeling is still limited
588 (e.g. Faccenda, 2014; Wilson et al., 2014), natural samples from high-pressure (this study)
589 and ultrahigh-pressure exhumed metamorphic terrains may preserve records of the
590 interactions of deep-fluids with the slab-forming rocks. In this study, it is shown how major
591 lithological interfaces (e.g. crust-metasediments) may represent ideal settings for fluid
592 channelization. In addition, the data presented here also show that Ca-Mg-rich rocks
593 (diopside-rich) and ultramafic rocks are reactive lithologies for rock carbonation at high-
594 pressure conditions.

595 Interaction between slab-derived fluids and mantle-wedge rocks also represents a
596 possible lithological configuration for rock carbonation. High amounts of carbonic fluids
597 resulting from slab carbonate dissolution are expected to percolate through the mantle wedge,
598 where ultramafic rocks may represent a suitable reactant (Kelemen and Manning 2015).
599 Based on the current knowledge of processes occurring along the plate interface (e.g.
600 Syracuse et al., 2010), carbonation of the hydrated mantle wedge overlying subducting slabs
601 seems unlikely in the case of vertical upward migration (rising T), whereas it is more
602 plausible along the slab-mantle interface (decreasing T). Exhumation of cold serpentinite
603 diapirs in forearc settings may also be a possible environment for rock carbonation (Fryer,
604 1992). Future studies on rocks ascribed to the mantle wedge are needed to test this hypothesis.

605 **9. Conclusions**

606 The petrological and geochemical results of this study indicate that the Corsican eclogite-
607 facies marbles found along major fluid conduits have a metasomatic origin and were formed
608 at high-pressure conditions during subduction. These rocks formed by carbonation of Ca-Mg
609 silicate rocks by percolating carbonic fluids (Fig. 9). This implies that carbonic fluids formed
610 during prograde carbonate dissolution may not be directly and fully transferred to the mantle
611 wedge, but can also flow along slab interfaces (i.e. crust-metasediments) and reprecipitate
612 carbonates under favorable conditions in both slab- and mantle-forming rocks. Carbonates
613 precipitating from these fluids then display a characteristic geochemical and isotopic
614 signature. Therefore, carbonation of Ca-Mg silicate rocks at high-pressure-low temperature
615 conditions can be an efficient process to lock carbon in the rock, as is well documented at
616 shallow and seafloor conditions (Guyot et al., 2011; Matter and Kelemen, 2009). The
617 widespread occurrence of these rocks in the units of Alpine Corsica is likely a consequence of
618 the overall exceptional preservation of pristine high-pressure-low temperature assemblages in
619 this belt. This suggests that analogous rocks and processes may have occurred in more

620 retrogressed high-pressure belts, such as the Western Alps, the Cyclades and Turkey, and may
621 be happening today in present-day subduction zones as well.

622 Whether or not high-pressure rock carbonation permanently binds carbon in the rock
623 cannot be easily established at present. For example, high-pressure carbonated rocks can
624 experience successive carbonate dissolution in deeper parts of subduction zones. Nonetheless,
625 carbonation of slab- and mantle-forming rocks (Fig. 9) likely modulates the residence time of
626 carbon in different reservoirs, and can modify the oxygen and carbon isotopic signature of
627 carbonates in subduction zones. Considering a longer time-scale perspective (e.g. time
628 elapsed from subduction initiation to continental collision), carbonation at high-pressure
629 conditions may ultimately influence the fluctuation of CO₂ emissions at volcanic arcs during
630 the life of a subduction zone, and thereby the fluctuation of atmospheric CO₂ over geological
631 time scales (e.g. Berner & Kothavala, 2001).

632
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643

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832 **Figure Captions**

833 **Fig.1:** Geological background of the study area. a) Simplified regional setting of Alpine Corsica (France) in the
834 Western Mediterranean region. Modified after Molli and Malavieille (2011). b) Simplified tectono-stratigraphic
835 map of Alpine Corsica. The black box indicates the position of the study area. c) Simplified geological map of
836 the San Petrone unit. Figures modified after Vitale Brovarone et al. (2013).

837
838 **Fig. 2:** simplified structural sketch summarizing the field relationships between the different rock types and the
839 location of the study samples. The star refers to metasomatic marbles formed at the expense of former
840 serpentinites.

841
842 **Fig. 3:** Representative textural features of metasomatic marble in the field. a) Crack-seal texture in a
843 metasomatic marble lens located in the metasomatic rind formed along the continental basement-serpentinite
844 contact. Dashed lines mark the schistosity in the host rock and the orientation of the remains of the host rock in
845 the carbonate-rich domain (see detail in b). Note that the silicate layers are deflected toward the carbonate vein.
846 b) Detail of carbonate layers containing rod-shaped aragonite pseudomorphs alternating with vein-parallel bands
847 of wallrock inclusions. c) Interdigitation of rod-shape carbonate with Stage#1 diopside-lawsonite rock. d)
848 Carbonate+omphacite vein cutting across Stage#1 diopside+lawsonite rock. The black dotted line marks the vein
849 wall and the green area overdrawn marks the selvage extension. e) and f) Photograph and related interpretative
850 sketch of a hydraulic breccia (types defined by Jébrak 1997) consisting of angular clasts of diopside+lawsonite
851 rock (Stage#1 metasomatism) sealed by a network of veins containing rod-shaped carbonate crystals. g and h)
852 Outcrop with high carbonate/silicate ratio and corresponding sketch. Rounded chunks of Stage#1 diopside-
853 lawsonite rock float in a carbonate matrix. Microtextures in the carbonate-rich domains suggest digestion and
854 chemical replacement of Stage#1 silicates by carbonate. Di=diopside; Lws=lawsonite.

855
856 **Fig. 4:** Progressive transformation of a precursor Stage#1 carbonate-free, diopside-lawsonite rock into a Stage#2
857 metasomatic marble. a) Stage#2 metasomatic marble cropping out along the serpentinite-metasediment contact.
858 The marble (grey) is interdigitated with the host Stage#1 diopside-lawsonite rock (green). The foliation of the
859 diopside-lawsonite rock (dashed line) can be followed in the carbonate layer. b) Thin section scan showing the
860 interdigitation texture of silicate and carbonate layers analogous to that documented at the outcrop scale in part
861 (a). Different degrees of carbonation are observed. White boxes indicate the location of the photomicrographs c,
862 d and e. c) Plane polarized light photomicrograph and corresponding sketch of the preserved portion of the
863 metasomatic diopside + lawsonite protolith; fan-shape diopside and lawsonite crystals statically crystallized. d)
864 Plane polarized light photomicrograph and corresponding sketch of the patchy distribution of carbonate pods
865 that characterizes a partially carbonated domain. Here, Stage#1 diopside aggregates are cut by the carbonate and
866 some fragments are preserved as relicts in carbonate layers. e) Plane polarized light photomicrograph and
867 corresponding sketch of a highly carbonated portion. Here the rock is transformed into a metasomatic marble;
868 prismatic carbonate crystals are well developed. A few remnants of Stage#1 diopside are preserved; these relicts
869 display embayed rims and atoll-like textures. In every sketch, Stage#1 diopside + lawsonite domains are
870 represented in green, whereas rod-shaped carbonate is in light beige.

871

872 **Fig. 5:** Backscattered electron (BSE) images obtained by SEM depicting micro scale textural relationships
873 resulting from fluid-rock interaction. a) BSE image of atoll-like Stage#1 diopside suggesting a digestion of a
874 silicate clast by carbonate; the Stage#1 diopsidic core is dissolved in favor of carbonate while a Stage#2 Na-Al
875 rich rim (omphacite) crystallized in textural equilibrium with the carbonate. Small fragments of diopside are
876 preserved as inclusions in carbonate crystals (red lines). b) BSE image of wallrock selvage shown in Figure 3d.
877 Diopside is overgrown by omphacite rim. Omphacite rims have the same composition as the vein infill
878 omphacite crystals (Table S1). c) Plane polarized light photomicrograph of diopside with aegirine-augite rim in
879 sample COR13-21d. Cal=calcite, Omp=omphacite, Di=diopside; Agt=aegirine-augite, Act=actinolite.

880

881 **Fig. 6:** Whole-rock chondrite normalized REE patterns (CI values from Sun and McDonough, 1989) for
882 metasomatic marbles (orange lines, see Fig. S3 for details), reference calcschist and ophicarbonates (solid and
883 dashed black lines, respectively), and Stage#1 diopside + lawsonite metasomatic rock (solid green line). The
884 shaded field represents the range of passive margin serpentinite whole-rock compositions (either actual or
885 metamorphic equivalent of Tethyan ocean floor; data from Barnes et al., 2014; Kodolányi et al., 2012).

886

887 **Fig. 7:** Carbon and Oxygen stable isotopic analyses of calcite. a) Calcite $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ plot of metasomatic
888 marbles (this study), blueschist and eclogite-facies marbles and calcite veins from other studies (Ague and
889 Nicolescu, 2014; Cartwright and Buick, 2000; Cook-Kollars et al., 2014; Galvez et al., 2013b). Only data for
890 non-metasomatic calcschists in Ague and Nicolescu (2014) and Galvez et al. (2013b) are reported. b) The rock
891 silicate mineral content vs. calcite $\delta^{18}\text{O}$ values. The dispersion of data illustrates the lack of correlation between
892 the light O isotopic signature and the silicate content. Analyses of reference calcschists and ophicarbonates are
893 also reported. We plotted data for samples that were also analyzed for their bulk rock composition (samples
894 COR13-32; COR13-30a; COR13-21b; COR13-21d; COR13-27e; COR13-17c; COR13-22c; COR13-28c; Table
895 S3). c) Metasomatic marble and reference calcschists $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ plot. Shaded areas correspond to
896 geochemical trend of carbonate affected by devolatilization (Bowman et al., 2009; Gerdes et al., 1995, 1999),
897 and carbonate reduction (Galvez et al., 2013b). Isotopic composition of carbonates affected by carbonate
898 dissolution is also reported (blue diamonds, Ague and Nicolescu, 2014).

899

900 **Fig. 8:** Carbon fluxes during subduction metamorphism. a) Bar diagram reporting the estimation of grams of
901 CO_2 release per 100 g of precursor rock during carbonate dissolution (Ague and Nicolescu 2014, blue bar) and
902 decarbonation reactions (Cook-Kollars et al., 2014, calculation by Perple_X software and natural sample
903 estimation, green and orange bars respectively) and grams of CO_2 bound per 100 g of precursor rock via
904 carbonate precipitation (red bar, this study). b) Contours of [C] in parts per million for aqueous fluid saturated in
905 CaCO_3 as a function of P and T. The red arrow indicates the P-T path of Alpine Corsica (Vitale Brovarone et al.,
906 2011a). The star corresponds to the $\Delta_{\text{cal-omp}}$ equilibrium temperature. The green field represents the predicted P-T
907 path for active subduction (D80 model, Syracuse et al., 2010). Figure adapted from Kelemen & Manning (2015).

908

909 **Fig. 9:** Schematic illustration showing the percolation of COH fluids parallel to the subducting slab. The
910 decreasing T and consequent decrease in carbonate solubility along this ascent path together with the interaction

911 with slab or mantle rock is a suitable context for carbonate precipitation via vein injection and mineral
912 carbonation.

913

914 **Table 1:** Whole rock major element composition of metasomatic marble, Stage#1 diopside+lawsonite rock
915 (OF3598) and Stage#1 rock with lawsonite>70% (COE5)

916

917 **Fig. S1:** Raman spectrum of aragonite inclusion in garnet.

918 **Fig. S2:** picture showing a detail of an omphacite-calcite vein. Omphacite grows from the vein wall toward the
919 center.

920 **Fig. S3:** Whole-rock chondrite normalized REE patterns (CI values from Sun and McDonough, 1989) for
921 metasomatic marbles, reference calcschist and ophicarbonates (solid and dashed black lines, respectively), and
922 Stage#1 diopside + lawsonite metasomatic rock (dashed blue line). The shaded field represents the range of
923 passive margin serpentinite whole-rock compositions (either actual or metamorphic equivalent of Tethyan ocean
924 floor; data from Barnes et al., 2014; Kodolányi et al., 2012).

925 **Table S1:** Representative clinopyroxene analyses.

926 **Table S2:** Whole rock composition of analyzed samples (major and selected trace elements). Analyses below
927 the lower detection limit are labeled "<d.l.". Values in wt.%.

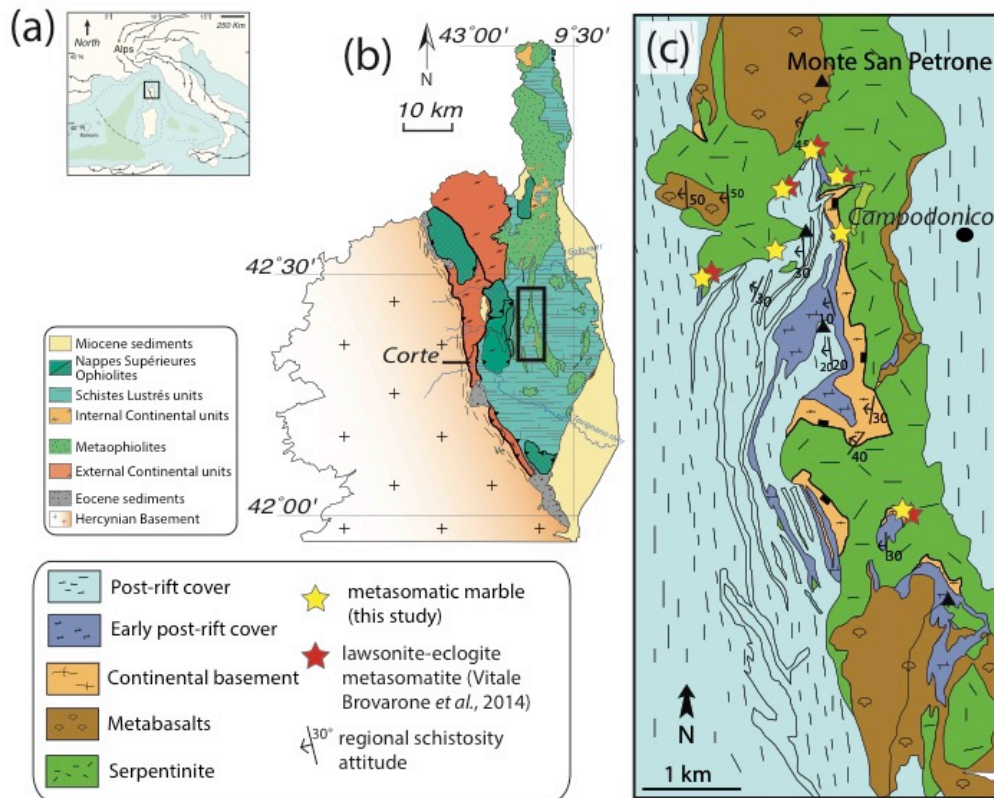
928 **Table S3:** Stable isotopes analyses of calcite. Analyses made in duplicate.

929 **Table S3.1:** Stable oxygen isotopes analyses of clinopyroxenes, average value of calcite filling vein and
930 calculated equilibrium T.

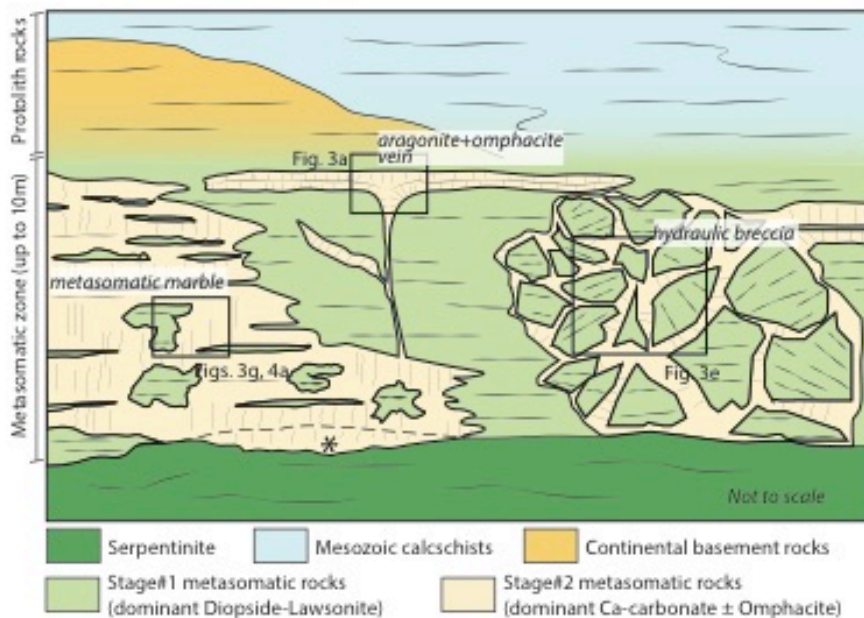
931 **Table S4:** Representative garnet analyses.

932 **Table S5:** Representative amphibole, lawsonite, phengite, pumpellyite analyses.

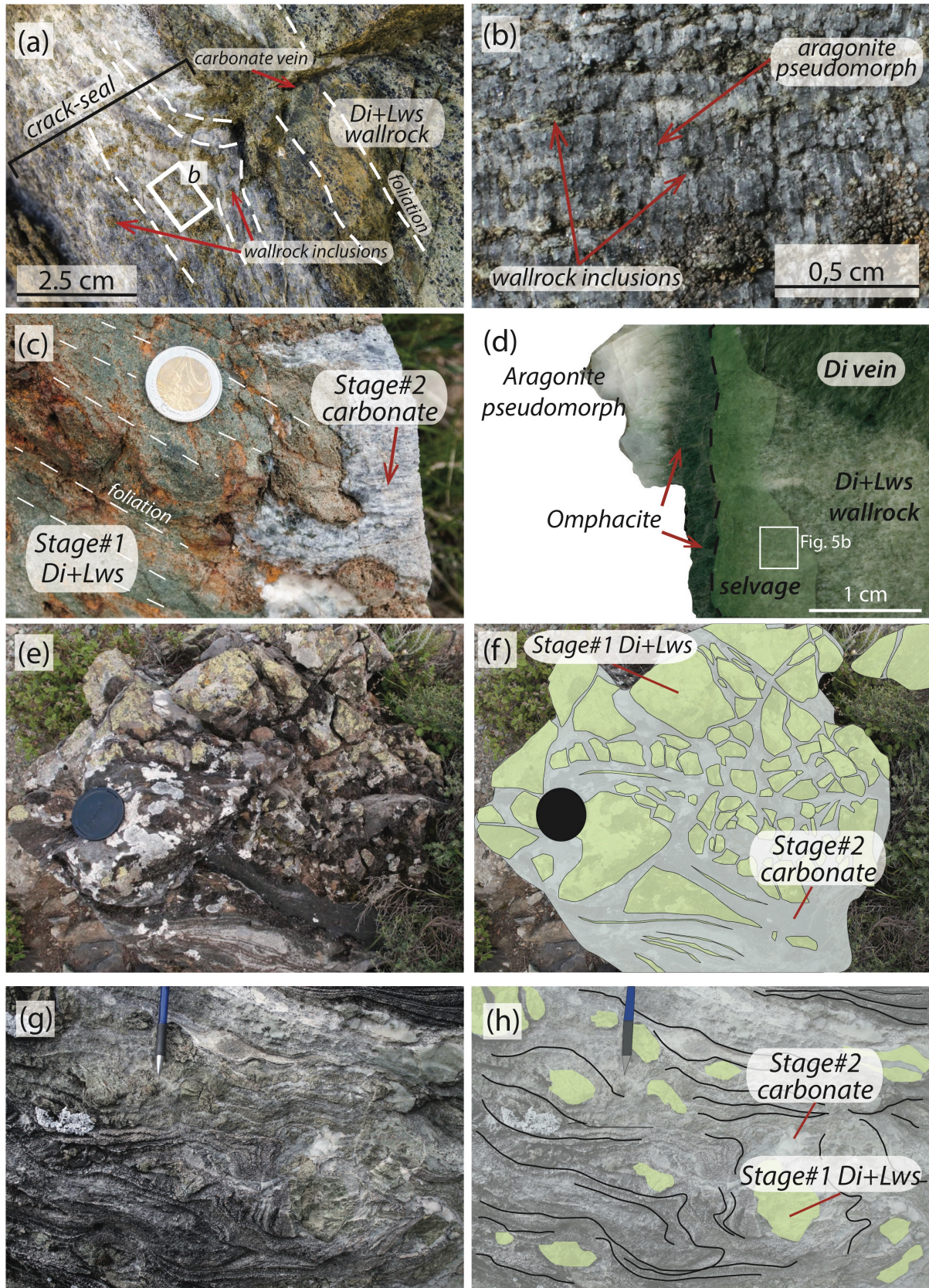
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934 Fig. 1

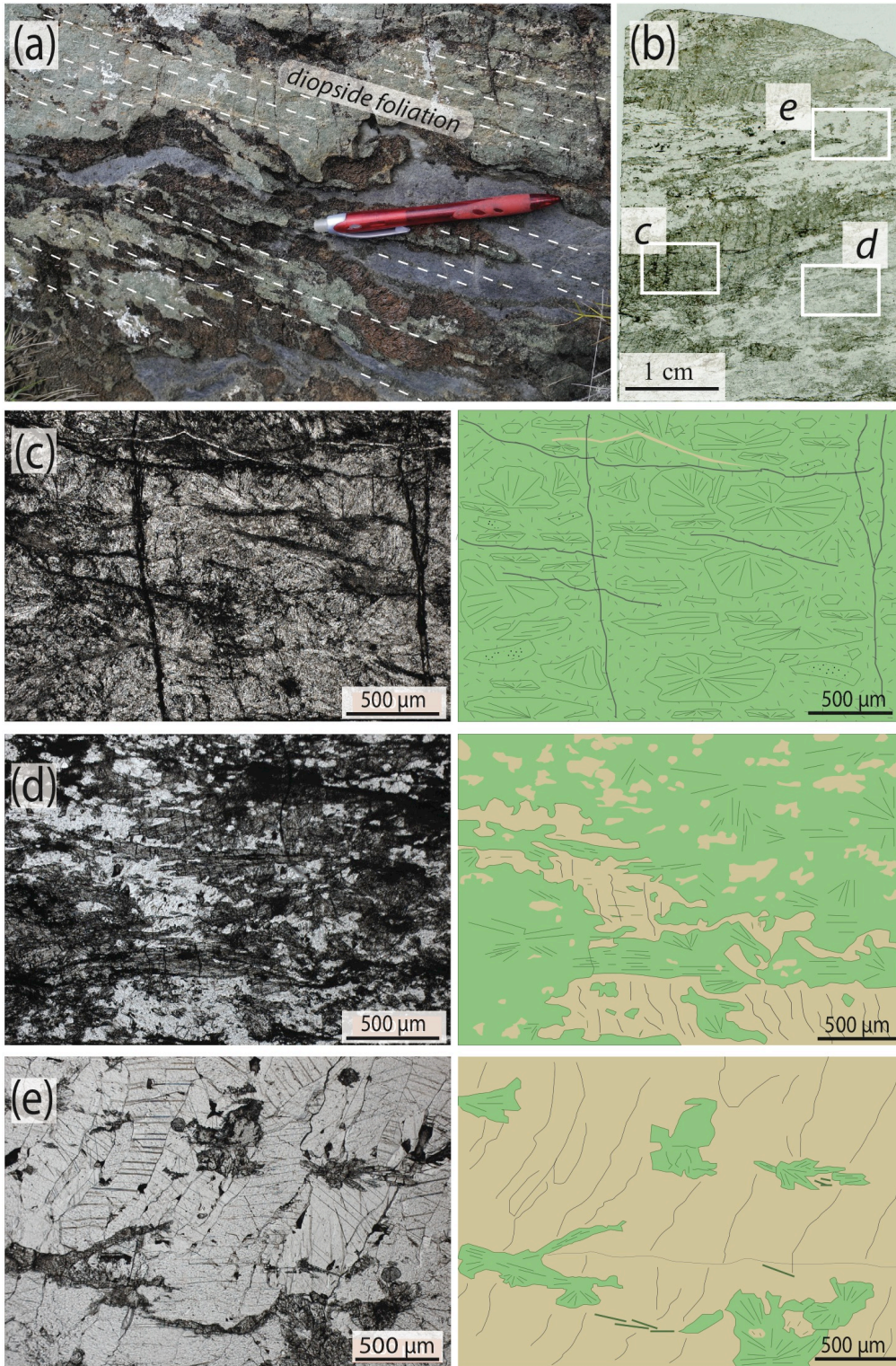


935 Fig. 2



936 **Fig. 3**

937

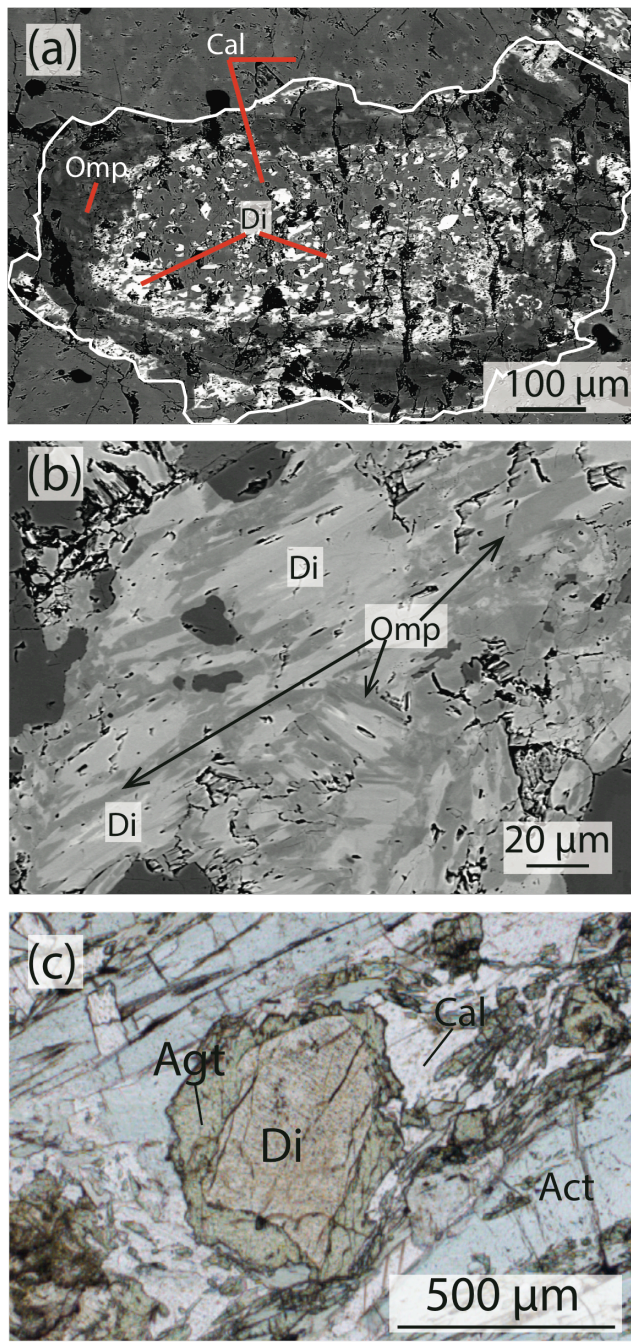


938 **Fig. 4**

939

940

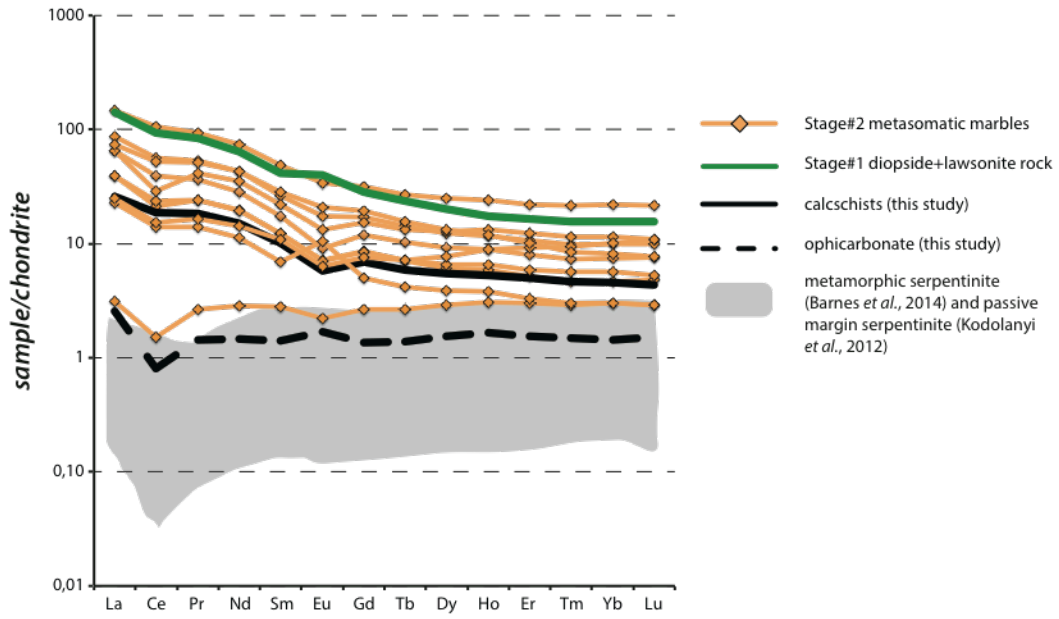
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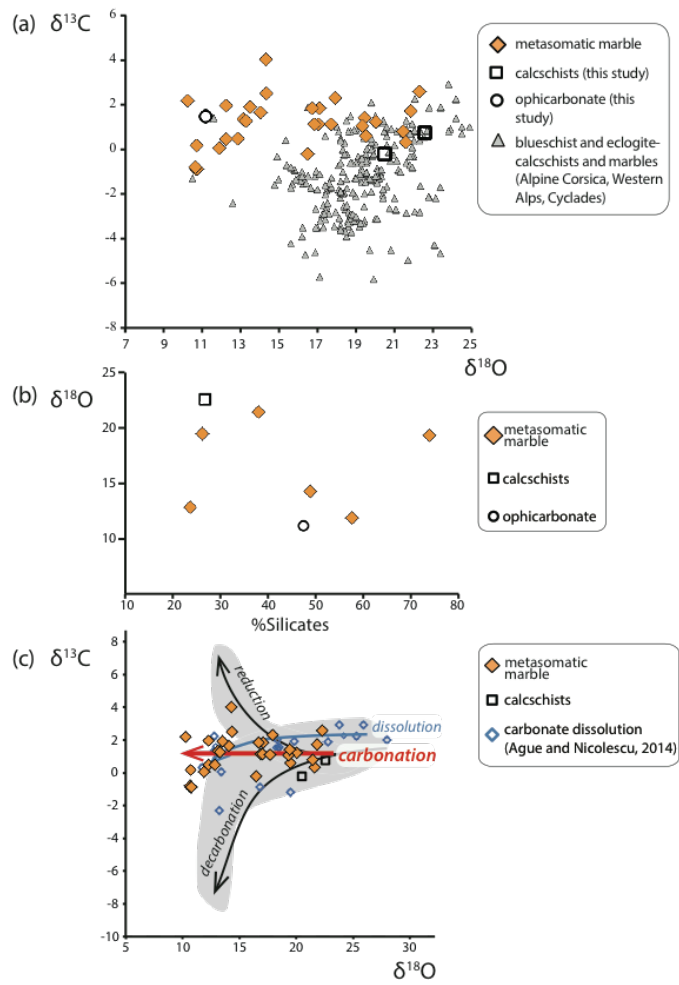
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943 **Fig. 5**

944

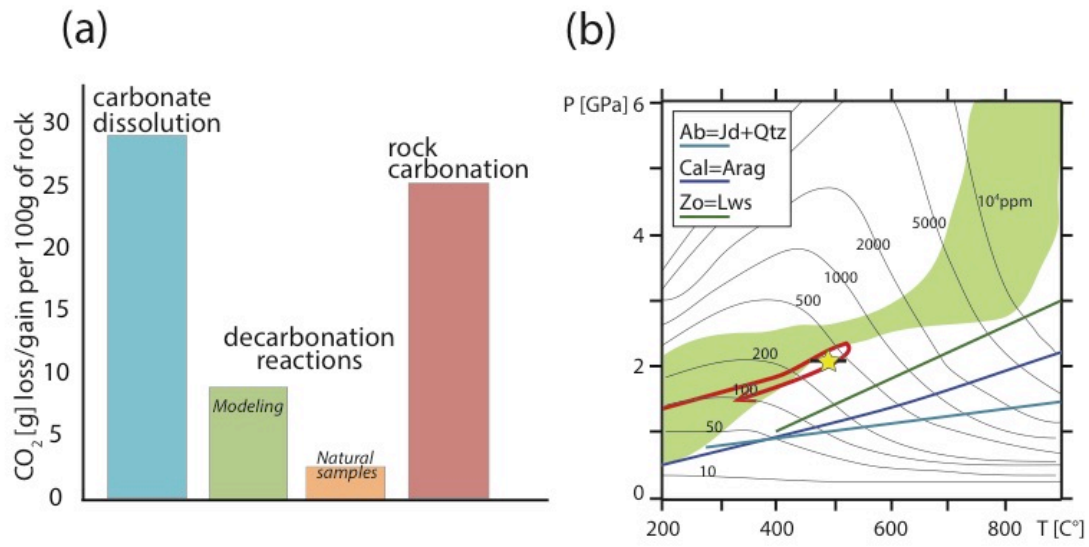


945 **Fig. 6**

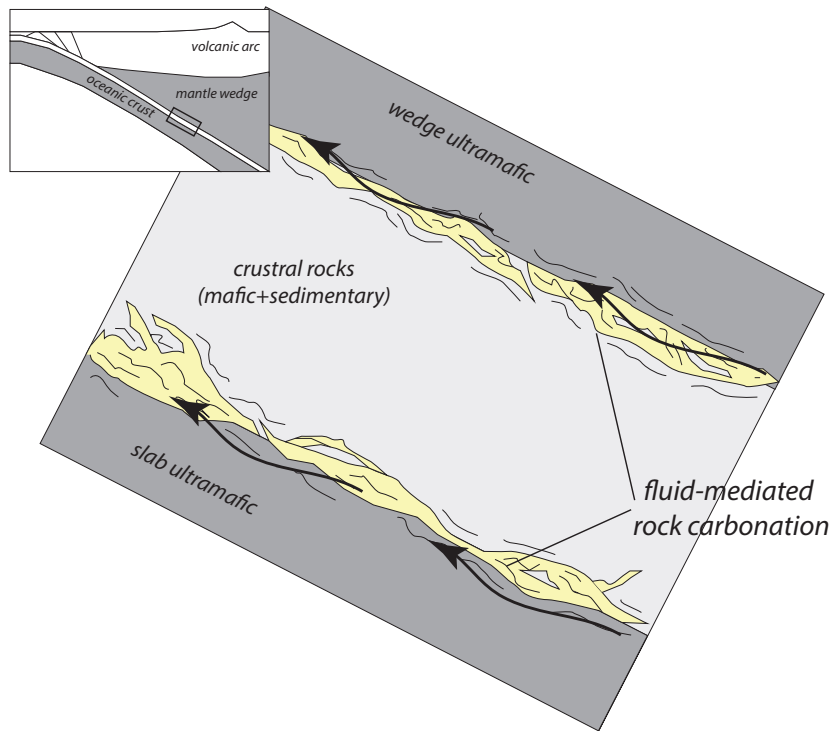


946 **Fig. 7**

947



948 **Fig. 8**



949 **Fig. 9**

Table 1: whole rock major element composition for metasomatic marbles (see Table S2 for details), Stage#1 diopside-lawsonite rock (OF3598) and Stage#1 rock with lawsonite>70% (COE5).

Sample	Metasomatic marble (n=4)	1 σ	OF3598 ^a	COE5 ^b
			Stage#1 rock	
SiO ₂	20.44	5.65	45.30	40.6
Al ₂ O ₃	4.97	2.94	15.11	25.6
Fe ₂ O ₃	3.22	1.14	5.03	2.28
MnO	0.18	0.16	0.11	0.13
MgO	3.14	1.77	6.95	1.8
CaO	39.23	5.32	20.62	17.65
Na ₂ O	0.92	0.95	0.47	0.51
K ₂ O	0.12	0.16	0.01	0.24
TiO ₂	0.18	0.11	0.65	1.94
P ₂ O ₅	0.09	0.04	0.11	0.41
LOI	27.05	5.12	5.57	7.94
Tot	99.54		99.94	99.10

^afrom Vitale Brovarone et al., 2014

^bfrom Martin et al., 2011