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Alberto Vitale Brovarone, Xu Chu, Laure Martin, Jay J. Ague, Patrick Monie, et al.. Intra-slab COH fluid fluxes evidenced by fluid-mediated decarbonation of lawsonite eclogite-facies altered oceanic metabasalts. *Lithos*, 2018, 304, pp.211-229. 10.1016/j.lithos.2018.01.028 . hal-01861178

**HAL Id: hal-01861178**

**<https://hal.science/hal-01861178>**

Submitted on 5 Dec 2020

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*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1661287> since 2018-03-05T17:16:01Z

*Published version:*

DOI:10.1016/j.lithos.2018.01.028

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## Q7 Intra-slab COH fluid fluxes evidenced by fluid-mediated decarbonation of lawsonite eclogite-facies altered oceanic metabasalts

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### 1 4 A R T I C L E I N F O

15 Article history:

16 Received 21 July 2017

17 Accepted 24 January 2018

18 Available online xxxx

20

42 Keywords:

43 C cycle

44 C fluxes at subduction zones

45 HP metamorphism

46 Subducted altered oceanic crust

47 Lawsonite-eclogites

48 Alpine Corsica

### A B S T R A C T

The interplay between the processes controlling the mobility of H<sub>2</sub>O and C-bearing species during subduction zone metamorphism exerts a critical control on plate tectonics and global volatile recycling. Here we present the first study on fresh, carbonate-bearing, lawsonite eclogite-facies metabasalts from Alpine Corsica, France, which reached the critical depths at which important devolatilization reactions occur in subducting slabs. The studied samples indicate that the evolution of oceanic crustal sequences subducted under present-day thermal regimes is dominated by localized fluid-rock interactions that are strongly controlled by the nature and extent of inherited (sub)seafloor hydrothermal processes, and by the possibility of deep fluids to be channelized along inherited or newly-formed discontinuities. Fluid channelization along inherited discontinuities controlled local rehydration and dehydration/decarbonation reactions and the stability of carbonate and silicate minerals at the blueschist-eclogite transition. Fluid-mediated decarbonation was driven by upward, up-temperature fluid flow in the inverted geothermal gradient of a subducting oceanic slab, a process that has not been documented in natural samples to date. We estimate that the observed fluid-rock reactions released 20–60 kg CO<sub>2</sub> per m<sup>3</sup> of rock (i.e. ~0.7–2.1 wt% CO<sub>2</sub>), which is in line with the values predicted from decarbonation of metabasalts in open systems at these depths. Conversely, the estimated time-integrated fluid fluxes (20–50 t/m<sup>2</sup>) indicate that the amount of carbon transported by channelized fluid flow within the volcanic part of subducting oceanic plates is potentially much higher than previous numerical estimates, testifying to the percolation of C-bearing fluids resulting from devolatilization/dissolution processes operative in large reservoirs.

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### 53 1. Introduction

54 Altered oceanic crust is a major carrier of C in subduction zones (dominantly as carbonate) (Staudigel, 2014), and its metamorphic evolution plays a critical role in controlling C fluxes to the deep mantle or back to shallow reservoirs, as indicated by several experimental (Hammouda, 2003; Poli et al., 2009; Keshav and Gudfinnsson, 2010; Poli, 2015), numerical (Kerrick and Connolly, 2001; Gorman et al., 2006; Collins et al., 2015) and field-based studies (Li et al., 2012, 2014; Collins et al., 2015).

The budget of carbonates at subduction zones depends on the interplay between processes producing carbonic fluids, such as decarbonation reactions, carbonate dissolution and melting, and those consuming carbon from the fluid in favor of carbonate precipitation, such as carbonation and veining. The role of decarbonation reactions (e.g. reactions between carbonates and silicates) on the carbonate budget of subduction zones has been extensively investigated by experimental and thermodynamic studies (Kerrick and Connolly, 2001; Gorman et al., 2006; Poli et al., 2009; Gonzalez et al., 2016). Carbonate dissolution (solubility of carbonate in a fluid at given pressure -P- and temperature -T-) has been only recently introduced to the common terminology of subduction-related processes (Frezza et al., 2011; Ague and Nicolescu, 2014; Faqç et al., 2014; Kelemen and Manning, 2015; Ferrando et al., 2017), and has been shown to play a major role in the

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76 production of carbonic fluids at forearc and subarc depths. Carbonate  
 77 melting is also an important process controlling the stability of carbon-  
 78 ates (Poli, 2015); it takes place at P-T conditions much higher than those  
 79 considered in this study, so is not discussed further. The carbonic fluids  
 80 produced by these processes may migrate towards shallower reservoirs  
 81 (i.e. mantle wedge, volcanic arcs) (Kelemen and Manning 2015 for  
 82 review), or reprecipitate as secondary carbonate in metamorphic  
 83 veins or during carbonation of silicates in the slab at high-pressure  
 84 (HP) conditions (Piccoli et al., 2016; Scambelluri et al., 2016).

85 All the above-mentioned processes are strongly enhanced by the  
 86 infiltration of aqueous fluids in carbonate-bearing rocks (Gorman  
 87 et al., 2006; Frezzotti et al., 2011; Ague and Nicolescu, 2014). The transition  
 88 from blueschist- to eclogite-facies metamorphic conditions  
 89 takes place in the forearc region of subduction zones (ca. 70–80 km),  
 90 and has long been shown to be the locus of important dehydration  
 91 reactions (e.g. breakdown of glaucophane and lawsonite in favor of  
 92 omphacite and garnet) releasing considerable amounts of aqueous  
 93 fluids (van Keken et al., 2011). The percolation of these fluids at  
 94 eclogite-facies conditions within the slab may therefore enhance fluid-  
 95 rock processes and modify the equilibria controlling the stability of  
 96 carbonates as either solid or fluid phases (Gorman et al., 2006; Ague  
 97 and Nicolescu, 2014; Gonzalez et al., 2016; Piccoli et al., 2016).

98 Natural HP rocks exhumed in mountain belts provide an important  
 99 means to study how the interplay between different CO<sub>2</sub>-producing  
 100 and -consuming processes affects the carbonate budgets during subduc-  
 101 tion of oceanic crust at the critical depth of 70–80 km where large  
 102 amounts of aqueous fluids are released. Moreover, natural samples  
 103 provide information on the mechanisms of fluid-flow (e.g. pervasive  
 104 vs. channelized), and on the structural/mineralogical control of geolog-  
 105 ical media and their effects on devolatilization processes (Molina et al.,  
 106 2004; Plümper et al., 2016). Natural examples featuring the role of  
 107 fluid flushing on carbonate dissolution in slab-forming rocks are  
 108 increasingly documented (Frezzotti et al., 2011; Ague and Nicolescu,  
 109 2014; Ferrando et al., 2017). Theoretical studies predict that also  
 110 decarbonation reaction and significant CO<sub>2</sub> release may be induced by  
 111 upward fluid infiltration at depths corresponding to the blueschist-  
 112 eclogite transition (Gorman et al., 2006). However, most field-based  
 113 petrological studies of HP/LT carbonate-bearing lithologies have focused  
 114 on closed systems pointing to little decarbonation at these depths  
 115 (Cook-Kollars et al., 2014; Collins et al., 2015). Field evidence for  
 116 decarbonation of subducted rocks by upward, up-T fluid flow during  
 117 eclogitization is lacking.

118 The goal of this study is to examine the interplay between oceanic  
 119 structural inheritance and fluid-rock processes including dehydration,  
 120 rehydration, decarbonation and carbonate dissolution, and their contri-  
 121 butions to the fate of carbonates in subducted altered oceanic crust.  
 122 Here we provide the first study of these processes on fresh lawsonite  
 123 eclogite-facies carbonated metabasalts by integrating field, textural,  
 124 geochemical and thermodynamic data from Alpine Corsica, together  
 125 with observations from weakly metamorphosed equivalents. Corsica  
 126 hosts exceptionally fresh lawsonite-bearing assemblages that are typi-  
 127 cally completely replaced by lower-P/higher-T, retrograde assemblages  
 128 in most HP-LT orogenic belts. Moreover, the preservation of primary  
 129 oceanic structures is widespread. Thus, Corsica represents a rare oppor-  
 130 tunity to study the pristine lawsonite eclogite-facies reactions driven  
 131 by up-T fluid flow in a down-going oceanic slab at the critical zone  
 132 (70–80 km depth) where important petrological processes are pre-  
 133 dicted for most past (since the Phanerozoic; Tsujimori and Ernst,  
 134 2014) and active subduction settings (Syracuse et al., 2010) (Fig. 1).

## 135 2. Geological setting

136 Corsica, France, is a part of the Alpine orogenic system now isolated  
 137 from the European mainland by the opening of two Tertiary basins,  
 138 namely the Ligurian-Provençal and the Tyrrhenian basins (Jolivet  
 139 et al., 1998; Malavieille et al., 1998; Malusà et al., 2015) (Fig. 2). The

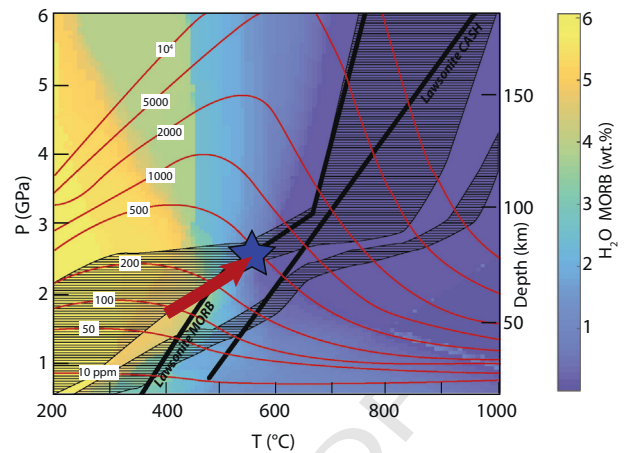
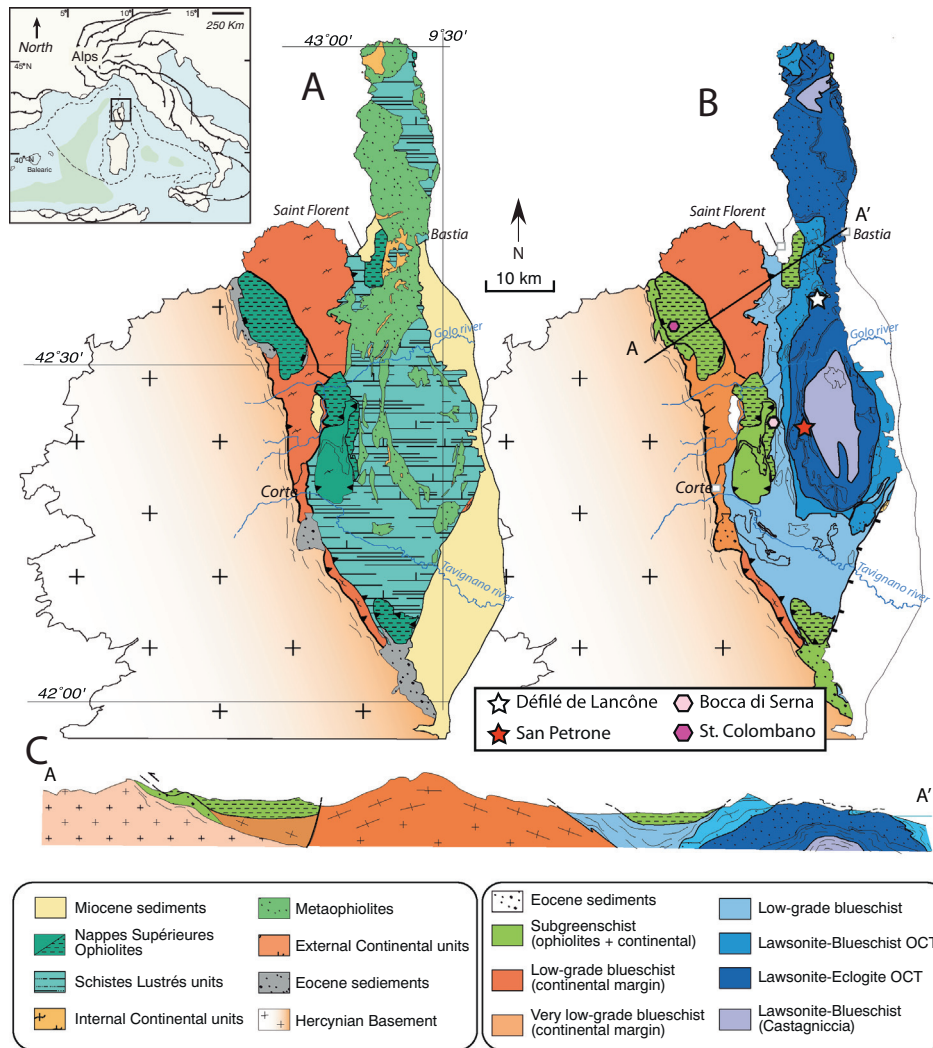


Fig. 1. P-T diagram showing the significance of the Corsican assemblages with respect to the modeled P-T path for active subduction zones (model D80; Syracuse et al., 2010), the patterns of carbonate solubility (C in ppm in aqueous fluids in equilibrium with CaCO<sub>3</sub>, Kelemen and Manning, 2015), and the breakdown boundaries of lawsonite in the Ca-Al-Si-O-H and MORB + H<sub>2</sub>O systems. The peak P-T estimates for the Corsica eclogites (star) are from Vitale Brovarone et al. (2011a). Note that the Corsica peak P-T conditions correspond to an important zone of dehydration in the MORB system at the blueschist-eclogite transition zone, which mainly relate to the breakdown of lawsonite in this system.

two main geological systems on the island are Hercynian Corsica and Alpine Corsica. Hercynian Corsica represents the largest part of the island and was only weakly affected by the Alpine orogeny, with the exception of the most external units of the Corsican paleo-margin (External Continental Units, Fig. 2A) that underwent blueschist-facies metamorphism during Alpine subduction. Alpine Corsica occupies the northeastern part of the island and mainly consists of Tethyan metaophiolites and metasediments of the Schistes Lustrés complex, equivalent to the Ligurian-Piemonte units of the Western Alps (Caron and Delcey, 1979; Lagabrielle and Lemoine, 1997; Vitale Brovarone et al., 2013). Weakly metamorphosed equivalents of these units are also exposed in the Nappes Supérieures (Rossi et al., 2002; Marroni and Pandolfi, 2003), and represent a good proxy for Tethyan ophiolites prior to Alpine metamorphism. The Schistes Lustrés complex comprises several units that preserve their primary Tethyan tectonostratigraphic coherence (mantle ultramafics ± metagabbros followed upsection by metavolcanics and metasedimentary cover rocks) but differ in their structural, lithological and metamorphic features (Lagabrielle and Lemoine, 1997; Vitale Brovarone et al., 2011a; Meresse et al., 2012; Vitale Brovarone et al., 2013, 2014) (Fig. 2). This study focuses on the Lawsonite-eclogite-facies unit. This unit consists of a well-preserved section of a Tethyan ocean-continent transition lithosphere (OCT) characterized by lithological suites similar to slow-spreading oceanic crust, such as serpentinites, metabasalts, and metagabbros (Jurassic), together with the characteristic presence of slivers of continental basement rocks interpreted as continental extensional allochthons (Vitale Brovarone et al., 2011a; Meresse et al., 2012; Beltrando et al., 2014). These rocks are capped by their primary Mesozoic metasedimentary cover rocks.

### 2.1. Metamorphic evolution of lawsonite eclogites in Alpine Corsica

The Alpine metamorphism in the Schistes Lustrés ranges from low-grade blueschist-facies (ca. 350 °C, 1.5 GPa) to lawsonite eclogite-facies conditions (ca. 530 °C, 2.3 GPa) (Fig. 1). A recent review of the available P-T estimates including a belt-scale thermometric dataset can be found in Vitale Brovarone et al. (2013) (see also Vitale Brovarone et al., 2014 for updates), and only the main metamorphic features of the lawsonite eclogite-facies terranes are reported in the following. Lawsonite eclogite-facies rocks in Alpine Corsica are well



**Fig. 2.** (A) Simplified geological map of Alpine Corsica. (B) Metamorphic map of Alpine Corsica. The stars in (B) refer to the two selected, eclogite-facies case studies, and the two low-grade equivalents.

178 preserved and include assemblages indicating the transition from  
 179 garnet blueschist to eclogite *sensu stricto* (omphacite-garnet-rich)  
 180 (Caron and Péquignot, 1986; Miller et al., 2000; Healy et al., 2009;  
 181 Ravna et al., 2010; Vitale Brovarone et al., 2011b; Vitale Brovarone  
 182 et al., 2014). A large thermometric dataset based on Raman spectroscopy  
 183 on the carbonaceous material (RSCM) in this unit points to the  
 184 peak T ranging from ~460 °C in the northern part to ~540 °C in the  
 185 southern part of the unit across the belt (Vitale Brovarone et al.,  
 186 2013). Abundant lawsonite and glaucophane inclusions in the eclogitic  
 187 garnet indicate prograde metamorphism at HP/LT conditions in the  
 188 lawsonite-blueschist facies. The peak, lawsonite-eclogite-facies assem-  
 189 blages in the metabasaltic suites are strongly controlled by the whole-  
 190 rock composition, with two main end-members being omphacite(s) +  
 191 lawsonite + garnet + titanite + phengite (eclogite-type) and amphi-  
 192 bole(s) + lawsonite + garnet + titanite + phengite (blueschist-type)  
 193 (Miller et al., 2000; Ravna et al., 2010; Vitale Brovarone et al., 2011b).  
 194 Local P-T estimates are available mainly from pseudosection modeling of  
 195 mafic rocks. In the Défilé de Lancône, pseudosections for meta-pillow ba-  
 196 salts yield T of about 450–500 °C and P in the range 1.9–2.6 GPa (Ravna  
 197 et al., 2010). In the Monte San Petrone, prograde (450 °C, 1.8 GPa; 480 °C  
 198 2 GPa) and peak (520 ± 20 °C; 2.3 ± 0.1 GPa) T conditions are slightly  
 199 higher than the Défilé de Lancône (Vitale Brovarone et al., 2011b), consis-  
 200 tent with the regional RSCM dataset.

201 Overall, the reconstructed prograde P-T evolution matches the range  
 202 of P-T paths for most active subduction zones by Syracuse et al. (2010)

(Fig. 1). The retrograde path of the Corsican eclogites is poorly 203  
 constrained, but the preservation of lawsonite suggests relatively cold 204  
 and/or static conditions. 205

The peak Alpine HP-LT metamorphism of the lawsonite-eclogite 206  
 terranes was dated at ca. 34 Ma by means of U-Pb zircon, Lu-Hf garnet 207  
 and Ar-Ar phengite geochronology (Brunet et al., 2000; Martin et al., 208  
 2011; Vitale Brovarone and Herwartz, 2013). Other estimates include 209  
 a Sm/Nd age of ~83 Ma (Lahondère and Guerrot, 1997) and a scattered 210  
 Ar-Ar dataset ranging from 40 to 65 Ma (Brunet et al., 2000), but these 211  
 estimates are likely not relevant for the metamorphism studied herein 212  
 (see discussion in Vitale Brovarone & Herwartz, 2013). 213

### 3. Observations from very low-grade carbonated basalts 214

In order to improve our understanding of the metamorphic evolu- 215  
 tion of carbonated metabasalts at HP conditions, we made observations 216  
 in weakly metamorphosed ophiolitic units from Alpine Corsica, the 217  
 Nappes Supérieures (Fig. 2). A detailed description of these low-grade 218  
 materials is beyond the scope of this study, and only the most represen- 219  
 tative features are reported here for the purpose of providing a general 220  
 view of the (sub)seafloor hydrothermal alteration of the Corsican rocks 221  
 prior to subduction. We selected metabasalts from both the San 222  
 Colombano pass (Balagne Nappe) (Marroni and Pandolfi, 2003) and 223  
 the Bocca di Serna pass (Vitale Brovarone et al., 2014). In both cases, 224  
 pillow basalts are well exposed and capped by radiolarian metacherts. 225

226 The Alpine metamorphic conditions did not exceed ca. 300 °C and  
 227 0.4 GPa (Vitale Brovarone et al., 2013). Metabasalts from both areas  
 228 exhibit widespread evidence of seafloor hydrothermal alteration  
 229 and carbonate precipitation, even though important mineralogical  
 230 variations are observed between the two localities.

231 In the San Colombano metabasalts (e.g. sample 2cor14-2), carbonate  
 232 is found as filling material in hollow pillows, resulting in characteristic  
 233 “heater-like” structures (alternating basalt ceilings and hollows filled  
 234 by carbonate) that are interpreted to form during progressive cooling  
 235 of pillow basalts and then filled by hydrothermal products (Fig. 3A; cf.  
 Q14 Ballard and Moore, 1977). These veins contain mostly calcite, together  
 237 with chlorite and minor quartz, sulfides, and fine-grained hematite.

238 In the Bocca di Serna basalts, a complex network of veins is found in  
 239 the lowermost portion of the exposed basalt section (Fig. 3B,C). The  
 240 veins (e.g. sample Cor16-62a) mainly consist of quartz, Ca carbonate,  
 241 epidote and albite. Epidote + quartz-bearing veins are late with respect  
 242 to albite-bearing veins, whereas carbonate is present in both vein genera-  
 243 tions. Both albite and epidote are present preferentially at the vein sel-  
 244 vages. In some portions of the basalt section (e.g. sample Cor16-62b),  
 245 these phases are more pervasively distributed and contain tiny hematite  
 246 crystals conferring a reddish color to the rock (Fig. 3D). These domains  
 247 possibly reflect the hydrothermal replacement of the host basalt  
 248 by newly formed silicates and carbonate. Evidence for massive sulfide  
 249 deposits in these low-grade units was not found; however, sulfide  
 250 deposits were exploited in gabbros close by the Bocca di Serna pass  
 251 (J.P. Santori, personal communication).

252 Fig. 4 shows two examples of inherited seafloor hydrothermal veins  
 253 from the low-grade terranes in comparison with some lawsonite  
 254 eclogite-facies analogues that will be described in detail in the  
 255 following.

#### 256 4. Lawsonite eclogite-facies metabasalts and distribution of 257 carbonated eclogites

258 Metabasalts are widespread in the lawsonite-eclogite-facies unit  
 259 and form large bodies locally extending for several tens of km. The sam-  
 260 ples selected for this study are from two localities: the Défilé de Lancône  
 261 and Monte San Petrone areas (Fig. 2, and S1 for structural relationships)  
 262 (Miller et al., 2000; Ravna et al., 2010; Vitale Brovarone et al., 2011a,  
 263 2011b). In the Défilé de Lancône, metabasalts form a thick sequence

(200 m) including various types of well-preserved pillow shapes 264  
 (bulbous, flattened, elongate and hollow pillow), pillow metabreccias 265  
 and hyaloclastites. The metabasaltic sequence lies on a large body of 266  
 serpentinized peridotites capped by a rather thin layer of highly sheared 267  
 metagabbros (Fig. S1). Altogether, these rocks form a largely complete 268  
 Tethyan crustal sequence now overturned in the Alpine stack. Discon- 269  
 tinuous lenses of metachert are observed and plausibly represent the 270  
 original sedimentary cover of the basement sequence, i.e. radiolarian 271  
 metachert. In the San Petrone area, a large, ~200 m thick body of 272  
 metabasalts rests above serpentinized peridotites containing rare pods 273  
 of metagabbro. The limited deformation along this contact, as well as 274  
 the lithostratigraphic consistency at the regional scale, has been 275  
 interpreted as the evidence for the preservation of a primary slow- 276  
 spreading crustal sequence where the volcanic suite directly rests on 277  
 top of exposed mantle rocks (Vitale Brovarone et al., 2011a; Beltrando 278  
 et al., 2014). 279

#### 4.1. Four groups of carbonated eclogites 280

Corsican carbonated metabasalts can be subdivided into four 281  
 groups based on the origin and distribution of the carbonate (Fig. 5): 282  
 (1) seafloor hydrothermal veins preserved in undeformed metabasalts 283  
 (Fig. 5A–B); (2) carbonated metabasalt sensu stricto (Fig. 5C, see 284  
 below for definition); (3) metamorphic veins and crack-seals crosscut- 285  
 ting metabasalts (Fig. 5D); and (4) deformed carbonate-bearing 286  
 metabasalts (undifferentiated; Fig. 5E). Late, greenschist-facies carbon- 287  
 ate veins are not considered in this compilation (Miller et al., 2001; 288  
 Miller and Cartwright, 2006). Groups (1) and (2) have lower-grade 289  
 equivalents in weakly metamorphosed units and represent remnants 290  
 of seafloor hydrothermal processes, whereas group (3) represents the 291  
 result of metamorphic processes at HP conditions. Most carbonated 292  
 metabasalts have a remarkably high amount of garnet compared with 293  
 the carbonate-free metabasaltic rocks in the study areas (20 vol% vs. 294  
 <10 vol% in carbonate-free metabasalts). In the Défilé de Lancône, 295  
 carbonate-bearing metabasalts are more abundant in the uppermost 296  
 part of the volcanic sequence (lowermost structural position in the 297  
 overturned sequence; Fig. S1A). In the San Petrone area (Fig. S1B), 298  
 carbonate-bearing metabasalts are more scattered, and no obvious 299  
 correlation between their distribution and the primary volcanic section 300  
 can be established. 301

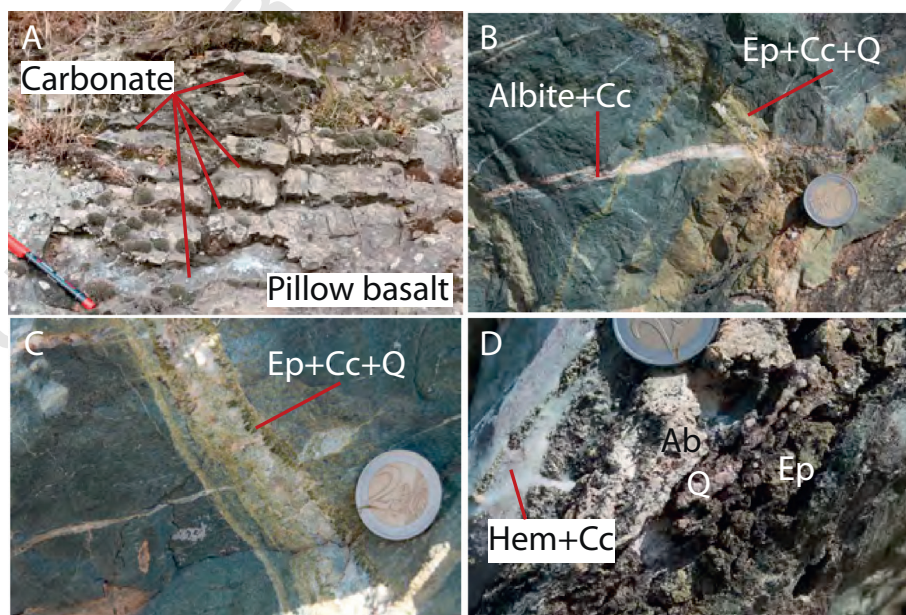
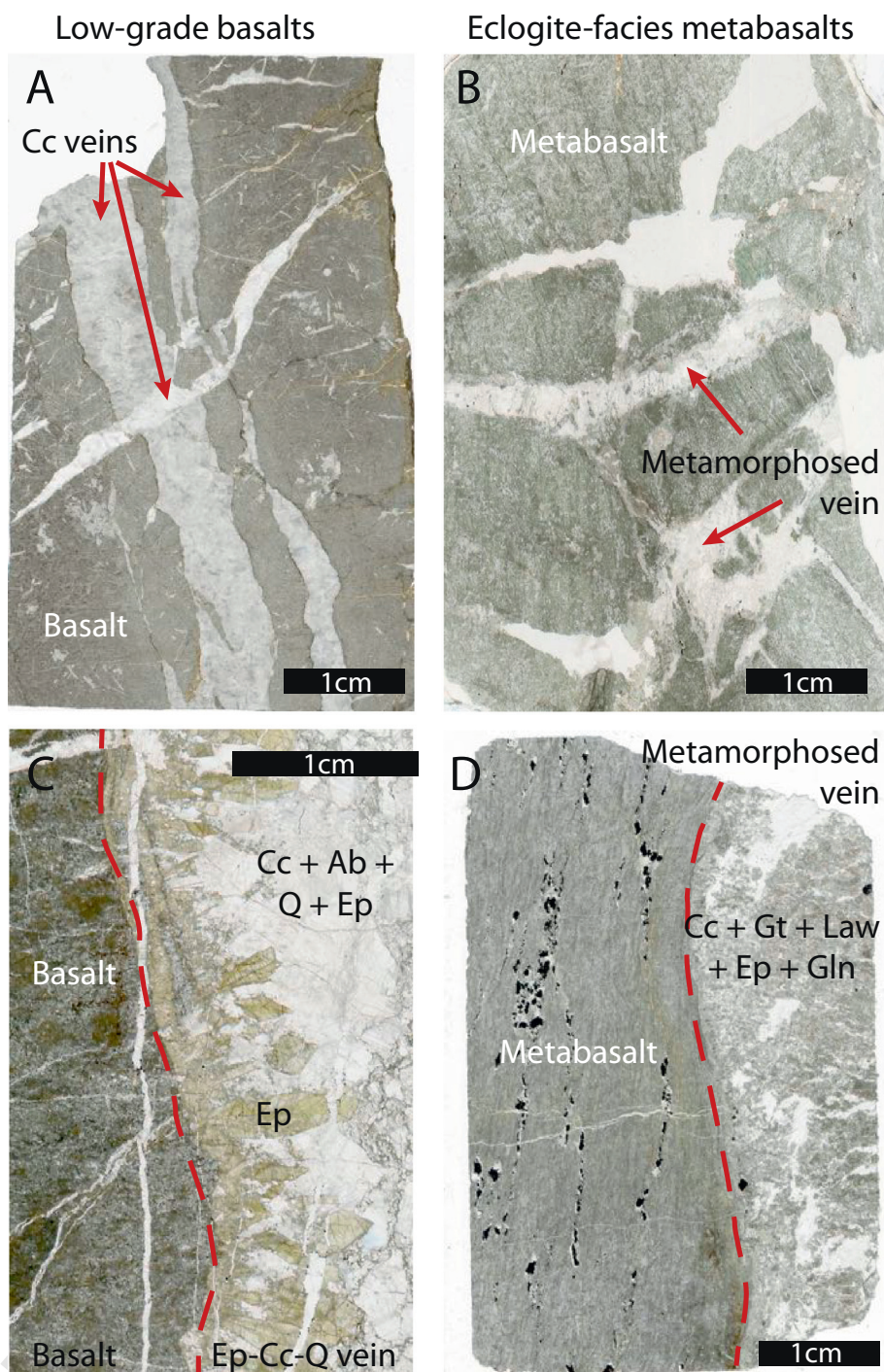


Fig. 3. Examples of hydrothermal alteration in weakly metamorphosed basalts. (A) Heater-like carbonate filling hollow pillows from the San Colombano area. (B–C) Epidote + carbonate + quartz + albite veins in the basalts from Bocca di Serna. (D) Pervasive carbonate + epidote + quartz + albite alteration of basalts from Bocca di Serna.



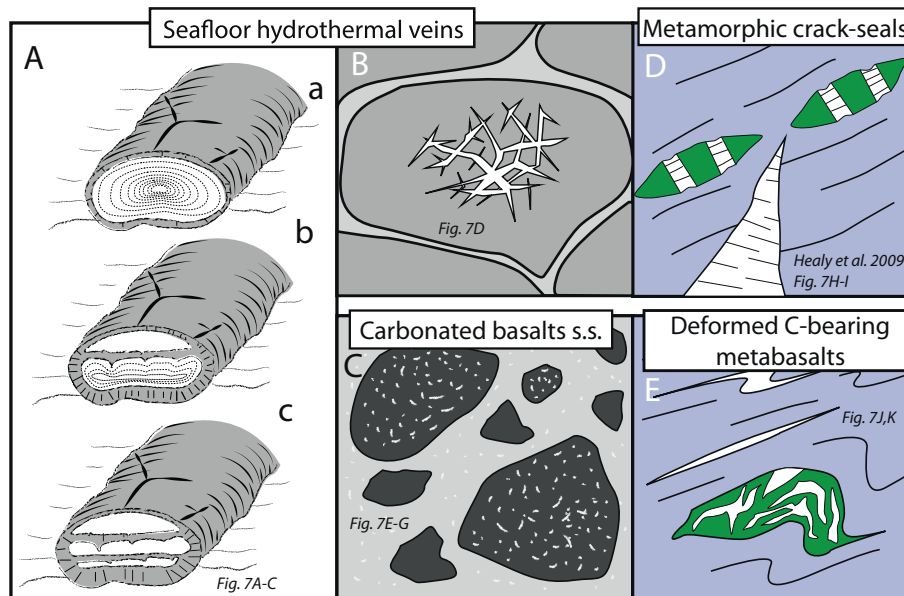
**Fig. 4.** Comparison between weakly metamorphosed (A, C) and eclogite-facies carbonate-bearing structures. (A) Carbonate-rich veins crosscutting the San Colombano basalts and (B) their equivalents in the San Petrone eclogites (sample OF3156). Note in (A) the presence of multiple vein generations. (C) Epidote + carbonate + quartz + albite veins in the Bocca di Serna basalts and (D) their metamorphosed equivalents in the Défilé de Lancône eclogites (sample Lancône-pillow). See text for detailed description and interpretations.

#### 4.1.1. Group 1: metamorphosed seafloor hydrothermal veins

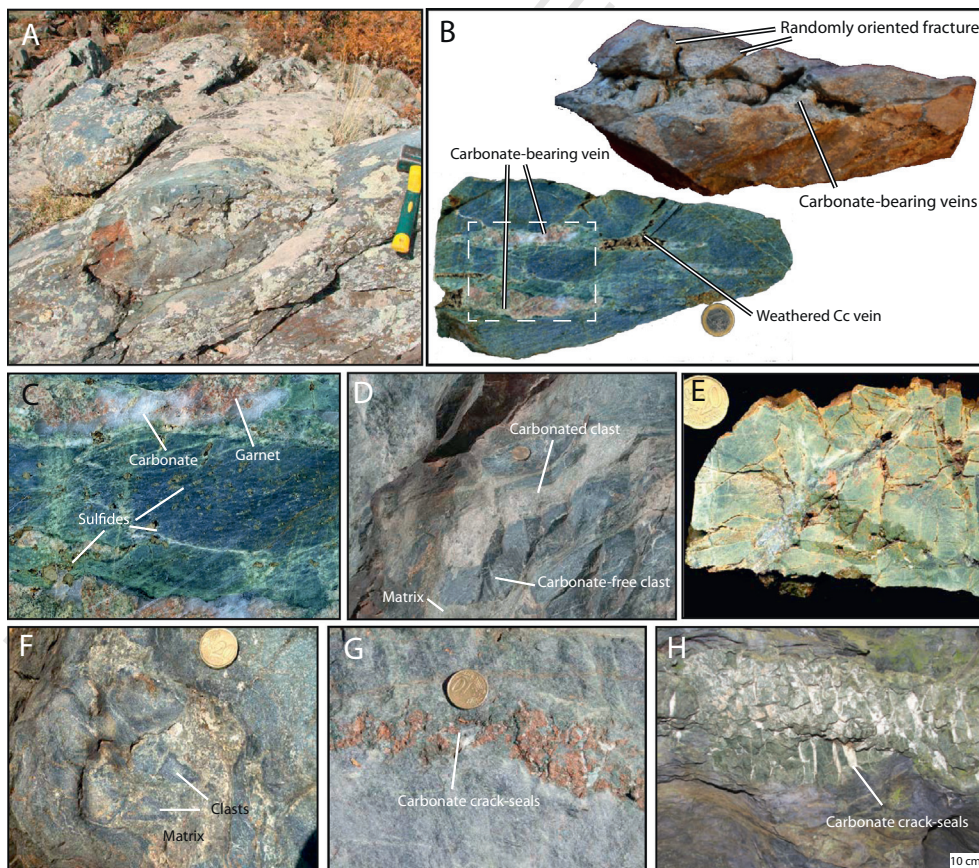
Different types of seafloor hydrothermal veins are distinguished (Figs. 4A, B, 6A–E). Some pillow metabasalts preserve the 'heater-like' structures characteristic of hollow pillows. These structures typically consist of cm-thick carbonate-rich parallel veins preserved in the pillow's core and extending outward to a more complex network of thinner, randomly oriented veins (Fig. 6B,C; see also Fig. 3A for low-grade precursor). In other cases, carbonate is only found as randomly-oriented veins filling igneous cooling fractures

in undeformed metabasalt (Figs. 4B, 5B, 6E). The carbonate in these structures may have two possible origins: hydrothermal carbonate precipitating from seawater circulation, or sedimentary carbonate filling open fractures. A hydrothermal origin is preferred for most of our samples based on the collected dataset (see sample description). Owing to surface carbonate dissolution, these rocks are rarely preserved on the weathered surface (Fig. 6E). Despite that, fresh samples were found both along the Défilé de Lancône in the interior of large pillow basalts, and at San Petrone.





**Fig. 5.** Cartoons summarizing the different types of carbonated metabasalts observed in Alpine Corsica. (A–C) represent inherited seafloor structures, whereas (D–E) are for either purely metamorphic (D) or undifferentiated (E) structures. (A) Mechanism of hollow pillow formation illustrating the origin of the ‘heater-like’ structures observed in the field; redrawn after Ballard and Moore (1977). In (a–c), the cavities are then filled by hydrothermal products such as carbonates (see also Fig. 6B,C). In (B), the carbonate veins are confined to the inner part of the pillow (see Figs. 4B, 6E). (C) Carbonated metabasalt s.s. This type of carbonate-bearing metabasalt is most commonly observed in basaltic metabreccias (see Fig. 6F for field examples). The carbonate distribution is pervasive and results from replacement of primary magmatic minerals, e.g., olivine. (D) Carbonate-bearing metamorphic crack-seals; filling material in boudinaged eclogite pods hosted in foliated blueschists, and discordant carbonate-bearing veins crosscutting the HP schistosity. (E) Cartoon illustrating different types of deformed carbonate-bearing metabasalts for which a clear origin (seafloor vs. subduction) is not obvious.



**Fig. 6.** Examples of Corsican carbonate-bearing metabasalts. Group 1: (A) Examples of preserved pillows metabasalts from the San Petrone area. Carbonates are present in the fractures in pillow's core. (B–D) Hollow pillow metabasalts from the Lancône valley. Note the main (horizontal) fractures extending laterally to a more complex network of fractures. In (C), note the abundance of garnet (reddish zones) within the carbonate-rich domains. (E) Example of weathered, randomly oriented, carbonate-bearing veins in the San Petrone metabasalts. The carbonate filled the open fractures. Group 2: (F) Carbonated metabasalts (*sensu stricto*) forming both clasts and matrix in pillow metabreccias. Group 3: (G–H) Carbonate + omphacite ± garnet ± phengite metamorphic crack-seals in the metabasalts from the San Petrone area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 320 4.1.2. Group 2: carbonated metabasalts sensu stricto

321 Carbonated metabasalts sensu stricto are herein distinguished from  
322 the other carbonate-bearing metabasalts. In these rocks, the carbonate  
323 is diffusely distributed in the matrix of undeformed metabasalts and  
324 is most probably the result of seafloor hydrothermal replacement of  
325 primary olivine or filling of disseminated vesicles (Alt and Teagle,  
326 1999), rather than crack-filling precipitation processes. These rocks  
327 are most typically found as metabasaltic clasts or matrix material in  
328 hyaloclastites or pillow metabreccias (Fig. 6F). Carbonated metabasalts  
329 sensu stricto are common along the easternmost part of the Défilé de  
330 Lancône metabasaltic suite.

#### 331 4.1.3. Group 3: carbonate-bearing metamorphic crack-seals

332 Carbonate-bearing metamorphic veins are locally abundant within  
333 the metabasaltic suite of the San Petrone area, whereas they are rarer  
334 in the Défilé de Lancône suite. Most of them were stretched and made  
335 subparallel to the main regional foliation, but some still show clear  
336 crosscutting relationships with the deformed metabasalt hosts (Healy  
337 et al., 2009; Ravna et al., 2010; Vitale Brovarone et al., 2011b). The  
338 typical assemblage consists of rod-shaped carbonate and omphacite,  
339 together with coarse-grained phengite; apatite and rare garnet can be  
340 easily identified in hand specimen.

#### 341 4.1.4. Group 4: deformed carbonate-bearing metabasalts

342 Owing to local intense deformation, the genesis of these rocks  
343 cannot be easily ascribed to one of the above groups. One type—quite  
344 common in the Défilé de Lancône area—exhibits a well-developed schis-  
345 tosity of alternating blue with light-blue/green layers. The variable  
346 thickness of the layers ranges from a few millimeters to several centi-  
347 meters. Carbonate in these rocks may also have a sedimentary rather  
348 than hydrothermal origin.

### 349 5. Sample description and mineral chemistry

350 In this section, we present the mineral assemblages, microstructures  
351 and mineral chemistry for the two key carbonated metabasalt types  
352 central to this study, i.e. metamorphosed seafloor hydrothermal veins  
353 (Group 1; three samples) and metamorphic crack-seals (Group 3;  
354 one sample). Ar–Ar data are also presented for phengite in Group 3  
355 metamorphic veins. A description of carbonated metabasalts sensu  
356 stricto (Group 2) and deformed carbonated metabasalts (Group 4) is  
357 beyond the aim of this work. Analytical methods are described in the  
358 **Q15** Supplementary Material.

#### 359 5.1. Group 1: Metamorphosed seafloor hydrothermal veins

360 Different types of primary hydrothermal veins are recognized, and  
361 show contrasting metamorphic transformations. The two most repre-  
362 sentative ones are described as follows.

##### 363 5.1.1. Large carbonate veins in pillow metabasalts

364 5.1.1.1. *Sample Lancône-pillow*. This sample was used for in-situ garnet O  
365 isotope analyses (see Section 6). It can be subdivided into two parts: the  
366 carbonate-free metabasalt host and a carbonate-rich hydrothermal vein  
367 (Fig. 6B,C). The host metabasalt mainly consists of glaucophane,  
368 lawsonite, actinolite, garnet, titanite, and sulfides, with garnet amount  
369 <5 vol%. These phases form a fine-grained, weakly deformed matrix  
370 that commonly preserves the original basaltic aphyric texture.

371 The carbonate-rich hydrothermal vein consists primarily of carbon-  
372 ate, garnet, and lawsonite, together with epidote, green-amphibole,  
373 chlorite, blue-amphibole, and sulfides (Fig. 7A).

374 Calcite is the dominant Ca carbonate polymorph in the rock. Never-  
375 theless, Raman spectroscopy revealed the preservation of aragonite  
376 included in garnet, lawsonite, and pyrite (Fig. S2), as also observed in  
377 the other selected samples (see also sample Lancône12-6). Garnet in

the carbonate veins is more abundant than in the host metabasalt 378  
(Fig. 7B), is present as isolated or aggregated crystals, contains inclu- 379  
sions of Ca carbonate, lawsonite, quartz, and epidote, and is partially 380  
replaced by late chlorite (Fig. 7C). The garnet compositional zoning 381  
is complex, and two main populations can be distinguished based on 382  
X-ray compositional mapping. The first one (Gt1; Fig. 7D) has an Mn- 383  
richer core [XSps = 0.2; XGrs = 0.4; XAlm = 0.4] and Mn-poorer rim 384  
[XSps = 0.0; XGrs = 0.7; XAlm = 0.3]. The second garnet generation 385  
(Gt2; Fig. 7E,F) is Mn-poor and displays a patchy compositional zonation 386  
with alternating Ca-richer [XGrs = 0.6; XAlm = 0.4; XSps = 0] 387  
and Ca-poorer [XGrs = 0.4; XAlm = 0.6; XSps = 0] compositions. 388  
In both garnet generations, a late Mn-rich shell is commonly observed. 389  
Epidote is widespread as both prograde inclusions in Gt2 (Ep1) and as 390  
a secondary phase after lawsonite (Ep2). Ep1 might also be preserved 391  
in the matrix. Lawsonite is found as inclusions in garnet and sulfides 392  
(Fig. 7F), and as large idiomorphic crystals in the matrix (Fig. 7A). Both 393  
lawsonite types formed at the expense of Ep1. Green-amphibole forms 394  
idiomorphic crystals and is present in higher modal proportion along 395  
the contact with the host metabasalt. Blue-amphibole forms isolated 396  
crystals dispersed in the calcite matrix, and is generally well preserved. 397  
Chlorite is common in the rock and is found as a prograde-to-peak phase 398  
and retrograde product after garnet or amphibole (Fig. 7C). Sulfides are 399  
extremely abundant in both the vein and the host metabasalt compared 400  
to the average metabasaltic rocks of Corsica; they are found as tiny crys- 401  
tals dispersed in the calcite matrix or as inclusions in garnet, lawsonite, 402  
and epidote. In the host metabasalt, sulfides are locally arrayed, suggest- 403  
ing precipitation along seafloor and/or metamorphic veins (Fig. 4D). 404  
Late albite is found as a retrograde product along cracks, grain bound- 405  
aries and in pressure shadows around sulfides (Fig. 4D). 406

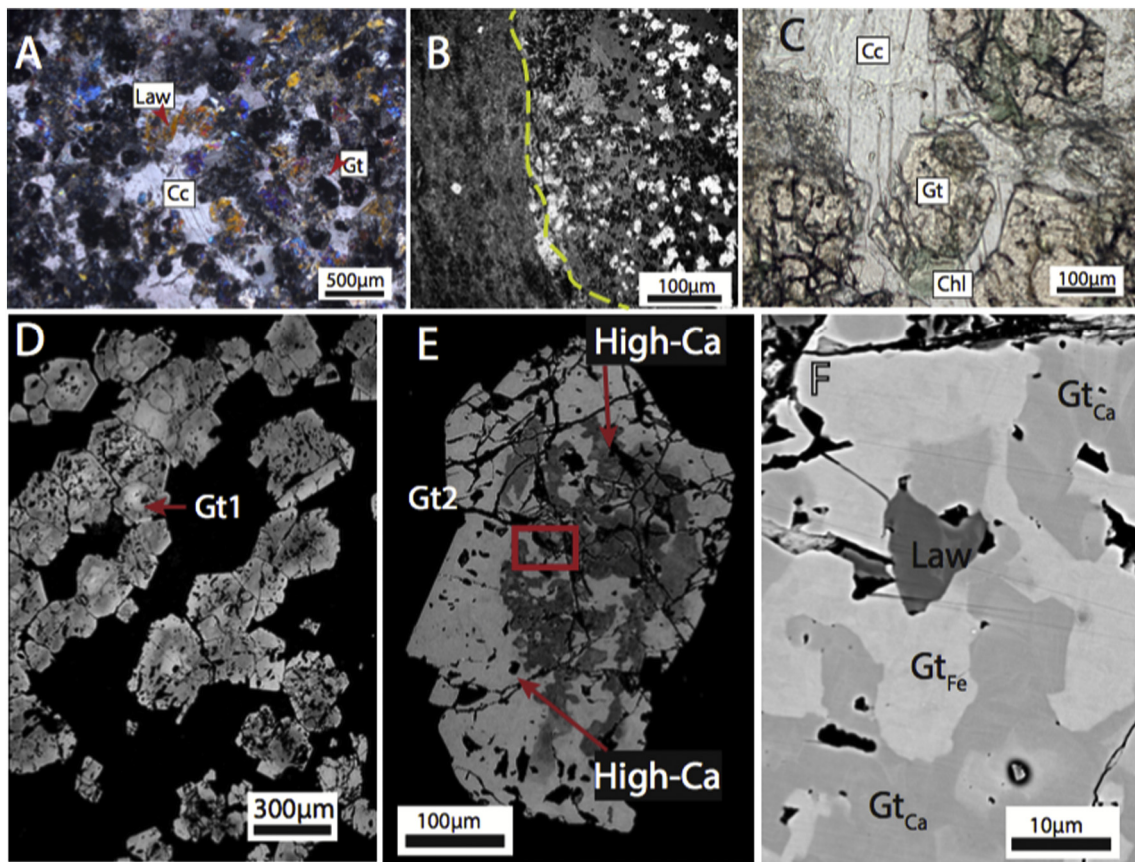
5.1.1.2. *Sample Lancône12-6*. This sample was used for thermodynamic 407  
calculations (see Sections 7 and 8). It was collected along the Défilé de 408  
Lancône, and belongs to a deformed large hydrothermal vein equivalent 409  
of sample Lancône-pillow (Fig. 6D). It has a homogeneous, fine-grained 410  
isotropic texture characterized by a light-colored matrix including small 411  
reddish garnet and variably oxidized sulfides. The main mineral phases 412  
are, in order of decreasing modal abundance, lawsonite, albite, garnet, 413  
calcite, epidote, amphiboles, chlorite, omphacite, quartz, titanite, pyrite, 414  
and apatite. 415

Lawsonite is well preserved and shows very little retrograde over- 416  
print (Fig. 8). It is common both in the rock's matrix and as inclusions 417  
in other phases, most notably garnet and pyrite (Fig. 8). In the matrix, 418  
lawsonite has a typical tabular idiomorphic habit, and includes mostly 419  
quartz with lesser carbonate. Lawsonite included in garnet may have 420  
different habits: it is idiomorphic when in close association with epidote 421  
(Fig. 8D,E), whereas it is xenomorphic and rounded in association with 422  
carbonate and quartz when included in garnet (Fig. 8F,G). 423

Carbonate is present as xenomorphic crystals, aggregates in the 424  
matrix, or as inclusions in other phases such as garnet (Fig. 8E–G), 425  
lawsonite (Fig. 8H), and pyrite. Like the previous samples, this rock con- 426  
tains Ca carbonate only, which is found as both matrix calcite and fresh 427  
aragonite inclusions (Fig. 8H). 428

Epidote is found in two main microstructural positions, (1) as 429  
inclusions in garnet (Ep1) [ $\text{Fe}^{3+} / (\text{Fe}^{3+} + \text{Al}) = 0.16$ ] (Fig. 8B); 430  
(2) as texturally late pseudomorphic products after garnet (Ep2a) 431  
[ $\text{Fe}^{3+} / (\text{Fe}^{3+} + \text{Al}) = 0.18$ ], matrix lawsonite (Ep2b) [ $\text{Fe}^{3+} / (\text{Fe}^{3+} + \text{Al}) =$  432  
0.07] (Fig. 8C) and, together with albite and chlorite, amphibole (Ep2c). 433  
Ep1 displays a complex zonation observed in backscatter (Fig. 8D,E). 434

Garnet forms poikiloblastic, idiomorphic to sub-idiomorphic crystals 435  
and aggregates. Single crystals range in size from about 100 to 500  $\mu\text{m}$ . 436  
Two end-member types of garnet can be distinguished. The first one 437  
(Gt1) includes clusters of lawsonite, aragonite, quartz and epidote 438  
(Fig. 8A,F,G). Gt1 is compositionally zoned, with zonation ranging 439  
from normal or inverse Mn bell-shaped zonation. The second one 440  
(Gt2) includes large Ep1 crystals and is chemically homogeneous 441  
[XGrs = 0.4; XAlm = 0.57; XSps = 0.02; XPy = 0.01] (Fig. 8B,I). The 442



**Fig. 7.** Photomicrographs of sample Lancône-pillow (Group 1: inherited hydrothermal vein). (A) Representative microstructure of the carbonate-rich hydrothermal vein showing abundant garnet and lawsonite in a calcite matrix. Cross-polarized light (XPL). (B) Backscatter electron (BSE) image of the interface between the metamorphosed carbonate channel (right) and the host metabasalt (left) in sample Lancône-pillow. Note the much greater abundance of garnet in the vein relative to the host metabasalt. (C) Late chlorite overprinting garnet. Plane-polarized light (PPL). (D) BSE image of zoned Gt1 in the inherited hydrothermal vein. The bright cores are Mn-richer, while the bright rims are Fe-richer. (E) BSE image of Gt2 alternating patches of Ca-richer and Ca-poorer compositions. (F) Detail of (E) (red box in E for location) showing the complex chemical zoning of Gt2. Note also a lawsonite inclusion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

443 relative modal amounts of the different garnet types vary from one to  
 444 another thin section. Garnet showing intermediate features between  
 445 Gt1 and Gt2 are also observed. Both garnet types locally include sulfides.  
 446 Zoned crystals of *amphibole* with glaucophane cores and actinolite rims  
 447 are widespread. Isolated actinolite crystals are also found, and may be  
 448 either a peak or a retrograde phase. *Chlorite* aggregates are deep green  
 449 and pseudomorphically replace garnet and amphibole. Chlorite has  
 450 Mg# of 0.56–0.58 (Mg/[Mg + Fe<sup>2+</sup>]). *Pyrite* forms sub-idiomorphic  
 451 crystals or aggregates, and includes lawsonite, carbonate, and quartz.  
 452 *Quartz* is common as inclusions in lawsonite, garnet, and pyrite  
 453 (Fig. 8C,E,F–G). In the matrix, quartz is scarce in the presence of Gt1,  
 454 but is more abundant in the vicinity of Gt2 (Fig. 8I). *Albite* is widespread  
 455 in this sample, and is present as large poikiloblastic crystals in the  
 456 matrix, as filling material in fractured garnet, or along grain boundaries  
 457 (Fig. 8I,G). In some cases, albite is found as inclusions in garnet (Fig. 8G).  
 458 However, the albite inclusions are systematically connected by late  
 459 cracks and are interpreted as a retrograde replacement of former inclu-  
 460 sions. Tiny *apatite* crystals are disseminated in the rock's matrix.

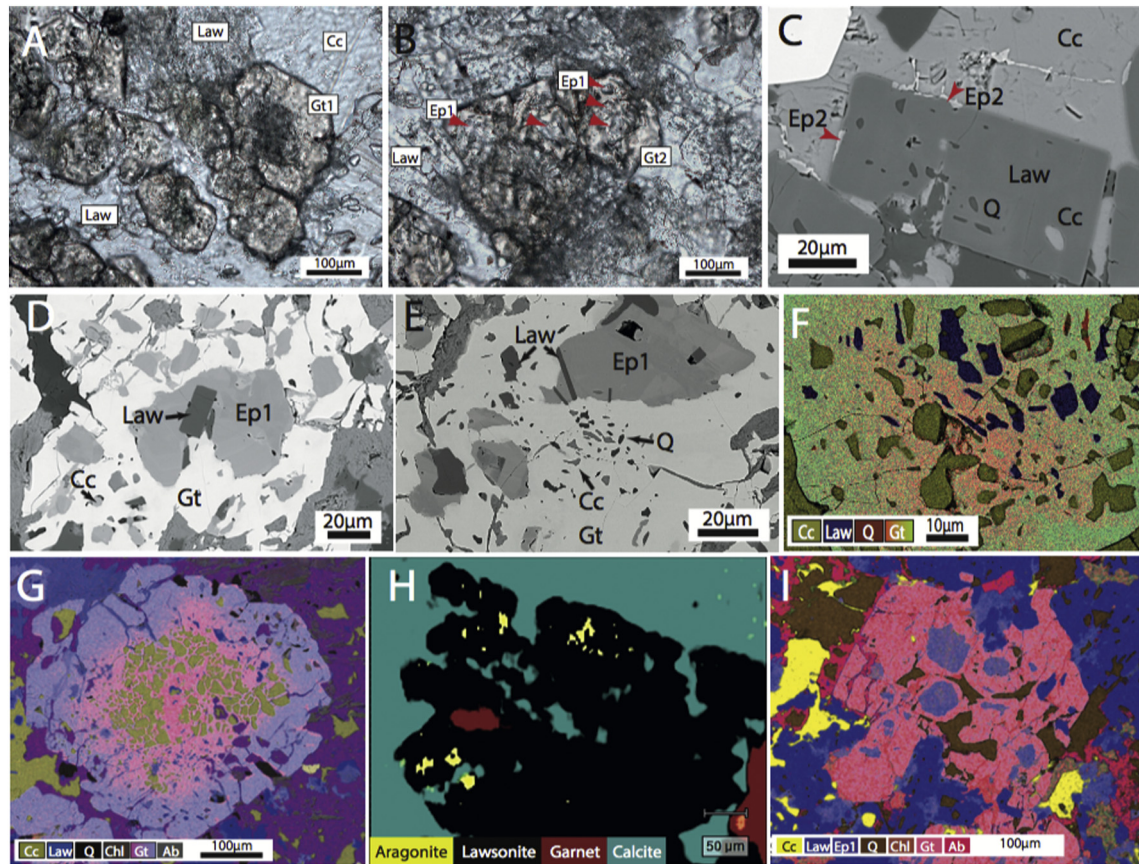
#### 461 5.1.2. Small carbonate veins in pillow metabasalts (sample OF3156)

462 Sample OF3156 belongs to the core of a well-preserved pillow  
 463 metabasalt. The metabasalt preserves primary igneous textures that  
 464 have been completely overgrown statically by a very fine-grained min-  
 465 eral assemblage typical of the lawsonite-eclogite facies (omphacite +  
 466 lawsonite + garnet) (Fig. 9A). Garnet in the host metabasalt is rare  
 467 and is crowded with tiny titanite inclusions. The carbonate-bearing  
 468 veins dominantly consist of calcite, together with lawsonite, omphacite,

and garnet (Fig. 9B–C). All vein minerals display a larger grain size com- 469  
 pared to the host metabasalt. In thin section, calcite exhibits concentric 470  
 square/pseudo-hexagonal shapes that plausibly represent preserved 471  
 aragonite basal sections now converted to calcite (Fig. 9B). Lawsonite- 472  
 rich selvages commonly formed at the contact between the carbonate- 473  
 bearing veins and the metabasalt wall (Fig. 9C), and may have 474  
 developed via either transformation of primary Ca-rich hydrothermal 475  
 products (e.g. epidote), or by the interaction between the carbonate 476  
 vein and the host metabasalt (decarbonation reactions) during subduc- 477  
 tion. Omphacite in the vein is zoned, with aegirine-richer cores and 478  
 omphacite-richer rims (Fig. 9C). The random vein orientation relative 479  
 to the Alpine regional structures is consistent with the hypothesis of 480  
 oceanic hydrothermal fracturing, but the reworking of these fractures 481  
 during HP fluid circulation cannot be excluded. 482

#### 5.2. Group 3: carbonate-bearing metamorphic crack-seals 483

The selected sample (OF3322) is characterized by two superimposed 484  
 veining events. The first vein generation is composed of massive garnets 485  
 and coarse-grained omphacite aggregates, whereas the second is dom- 486  
 inated by Ca carbonate, phengite, and minor omphacite (Fig. 10). A 487  
 detailed description of the first vein generation is beyond the aim of 488  
 this study and has been already given in previous works (Healy et al., 489  
 2009; Vitale Brovarone et al., 2011b). The chronological relationships 490  
 between the two veining events are clearly depicted by intense 491  
 hydrofracturing of garnet and omphacite and sealing by Ca carbonate 492  
 and phengite (Fig. 10C,D). A second generation of omphacite forms 493



**Fig. 8.** Representative microstructures of sample Lancône12-6 (Group 2: carbonated metabasalt *sensu stricto*). (A) Example of Gt1. Note the clouded core containing abundant rounded carbonate inclusions (see also panel G). (B) Example of Gt2. See also Figure I. (C) BSE image showing an idioblastic lawsonite crystal including quartz and carbonate. In some crystals, the carbonate included in lawsonite is still fresh aragonite (Fig. S2). Note also the development of Ep2 along the edge of the lawsonite crystal. (D–G) Examples of inclusions in Gt1. In (D) note the presence of an idioblastic lawsonite crystal growing on Ep1, both included in Gt1. This texture suggests a prograde partial conversion of epidote into lawsonite prior or during the garnet growth. (F–G) Composite X-Ray compositional maps showing the characteristic textures of Gt1 in sample Lancône12-6. In (G), note the abundant carbonate inclusions in Gt1 core. The garnet zoning is mainly due to variations in Mn, which is richer in the core and poorer in the rim. In both maps, note the included assemblage consisting of xenomorphic carbonate, quartz and lawsonite suggesting the garnet-forming reaction (1). (H) Raman map showing the preservation of fresh aragonite as inclusions in both lawsonite and garnet, and a complete conversion into calcite in the matrix. (I) Compositional map of Gt2 in sample Lancône12-6. Note the lack of significant zoning in this garnet type, the presence of atoll-like inclusions of Ep1, and the presence of matrix quartz in association with Gt2. Note also the presence of late albite. Abbreviations: Law: lawsonite; Q: quartz; Ab: albite; Cc: Ca carbonate; Gt: garnet; Chl: chlorite; Ep: epidote.

Q3 Q2

494 small, idioblastic crystals dispersed in the carbonate matrix. Phengite  
495 has a high Si content (Si = 3.5–3.6 atoms per formula unit, based on  
496 11 oxygens, Table 2). The association of high-Si phengite, newly formed  
497 omphacite and the overall freshness of the early garnet and omphacite  
498 assemblage altogether support the hypothesis of carbonate precipitation  
499 at HP conditions. Rarely, the phengite crystals are replaced by late  
500 albite, indicating at least some degree of retrogression.

501 We performed Ar–Ar geochronology on phengite from these veins.  
502 Single crystals of highly substituted phengite (Si = 3.5–3.6 a.p.f.u.)  
503 were separated from two different samples (M9-53a and M9-53b,  
504 equivalent to samples 2cor12-8, 2cor12-11 and OF3322) and analyzed  
505 by the step-heating method. The results are shown in Fig. 11 and  
506 Supplementary Table 1. The first sample is characterized by an initial  
507 slight stepping-up spectrum from  $26.8 \pm 1.3$  Ma to  $28.5 \pm 0.2$  Ma,  
508 followed by a well-defined plateau at  $29.2 \pm 0.6$  Ma. The second sample  
509 yields age spectra characterized by a plateau age at 25 Ma ( $25.3 \pm 0.5$   
510 and  $25.0 \pm 0.7$  Ma on two separate crystals).

## 511 6. Whole-rock and in-situ C and O stable isotopes

512 We performed whole-rock carbonate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  analyses on four  
513 samples from the Défilé de Lancône and San Petrone areas (Table 1),  
514 as well as in-situ  $\delta^{18}\text{O}$  garnet isotope analysis by SIMS in order to

investigate the possible contribution of decarbonation reactions to the  
isotopic signature of newly-formed Ca-rich garnet.

516  
517 Tables 3 and S2 and Figs. 12 and 13 show the results in per mil (‰)  
518 with respect to the international PDB standard for C and SMOW for  
519 oxygen. The hydrothermal veins from the Défilé de Lancône (e.g. sample  
520 Lancône-pillow) have  $\delta^{13}\text{C}_{\text{PDB}}$  of  $-1$  to  $-0.5\%$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  of  $9\%$ .  
521 The carbonated metabasaltic clast (sample Lancône12-6) has  $\delta^{13}\text{C}$  of  
522  $1\%$  and  $\delta^{18}\text{O}$  of  $11.6\%$ . Finally, the carbonate-bearing eclogitic crack-  
523 seals (samples OF3322, 2cor12-8 and 2cor12-11) have  $\delta^{13}\text{C}$  of  $1.2\%$   
524 and  $\delta^{18}\text{O}$  of  $11.6\%$ . The  $\delta^{13}\text{C}$  values are comparable with the lowermost  
525 values obtained by Miller et al. (2001) in Corsican eclogite-facies  
526 metabasites ( $-1$  to  $3\%$ ) (Fig. 12A). Conversely, the  $\delta^{18}\text{O}$  values are  
527 lower than the samples analyzed by Miller et al. (2001) ( $13$  to  $20\%$ ).

528 For in-situ  $\delta^{18}\text{O}$  garnet analyses, we selected garnet crystals with  
529 alternating Ca-poorer and Ca-richer zones (patchy, Mn-poor Gt2,  
530 Fig. 12B) in sample Lancône-pillow. Sixty point-analyses were per-  
531 formed in cut thin sections on six garnet crystals, and yield average  
532  $\delta^{18}\text{O}$  values of  $5.1 \pm 0.4\%$  ( $2\text{SD}_{\text{O}n} = 41\text{O}$ ) and  $4.83 \pm 0.4\%$   
533 ( $2\text{SD}_{\text{O}n} = 19\text{O}$ ) for the Ca-poorer and Ca-richer garnets, respec-  
534 tively (Fig. 12C). Using bulk Ca carbonate and in-situ garnet  $\delta^{18}\text{O}$  values  
535 for sample Lancône-pillow, and the oxygen fractionation factors by  
536 Zheng (1993), a T of  $\sim 500$  °C was obtained for the carbonate-garnet  
537 equilibrium, which is consistent with other temperature estimates in  
538 this area.

Q16 Q17

Q18

538

## 7. Garnet formation and decarbonation reactions

539

We investigated in more detail the most likely garnet-forming reactions and their contributions to the C budget of the rock. The metamorphic evolution of this sample is summarized in Fig. 13. The large variety of garnet compositions and mineral inclusions in our samples suggest local-equilibrium domains imposed by the precursor textures and mineralogy of the hydrothermally-altered basalt.

Gt1 in Group 1 samples Lancône-pillow and Lancône12-6 contains xenomorphic inclusions of lawsonite, aragonite, quartz ± Ep (Fig. 8E–G). The relict reactants included in the garnets thus suggest the reactions:

550  
551

553

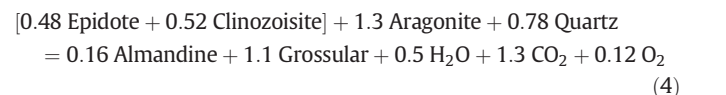
The common presence of quartz as inclusions in garnet and the textural dependence of Gt1 and Gt2 development on the availability of local quartz are consistent with these prograde reactions. The relative contributions of reactions (1) and (2) in the sample are variable, and depend on the extent of local re-equilibration of the sample (i.e. Ep1 to lawsonite) prior to garnet formation. Gt2 is texturally associated with Ep1 (Fig. 8I), and the chemical homogeneity of Gt2 and Ep1 suggests that the two phases have reached equilibrium by exchanging compositions via Reaction (2) and the redox reaction:



563

In this reaction, O<sub>2</sub> is included only as a redox indicator, but not considered as a fluid species in mass balance analysis due to its infinitesimal concentration.

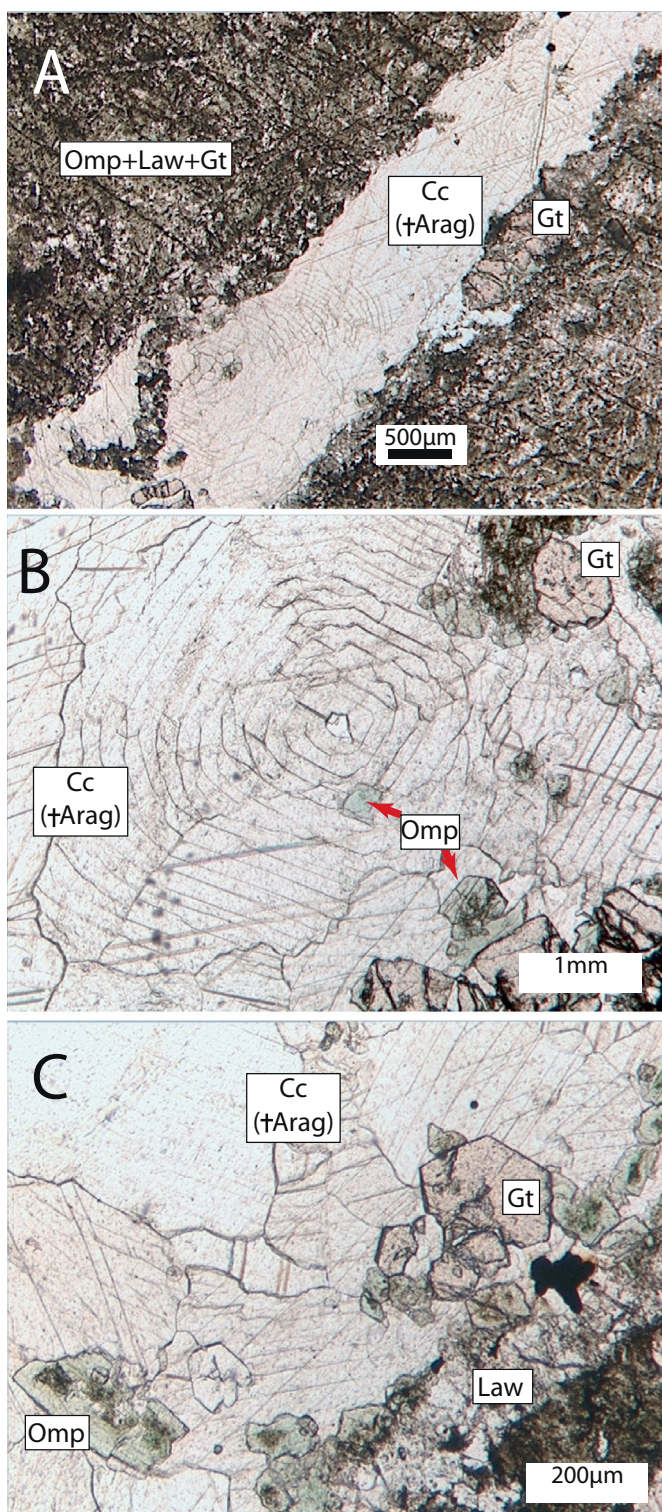
The presence of Mn- and Fe-rich garnet zones indicates that at least one additional mafic mineral, likely prograde chlorite, participated in the garnet-forming reactions. Reactions (2) and (3) can be coupled to account for the measured composition of Ep1 included in Gt2:



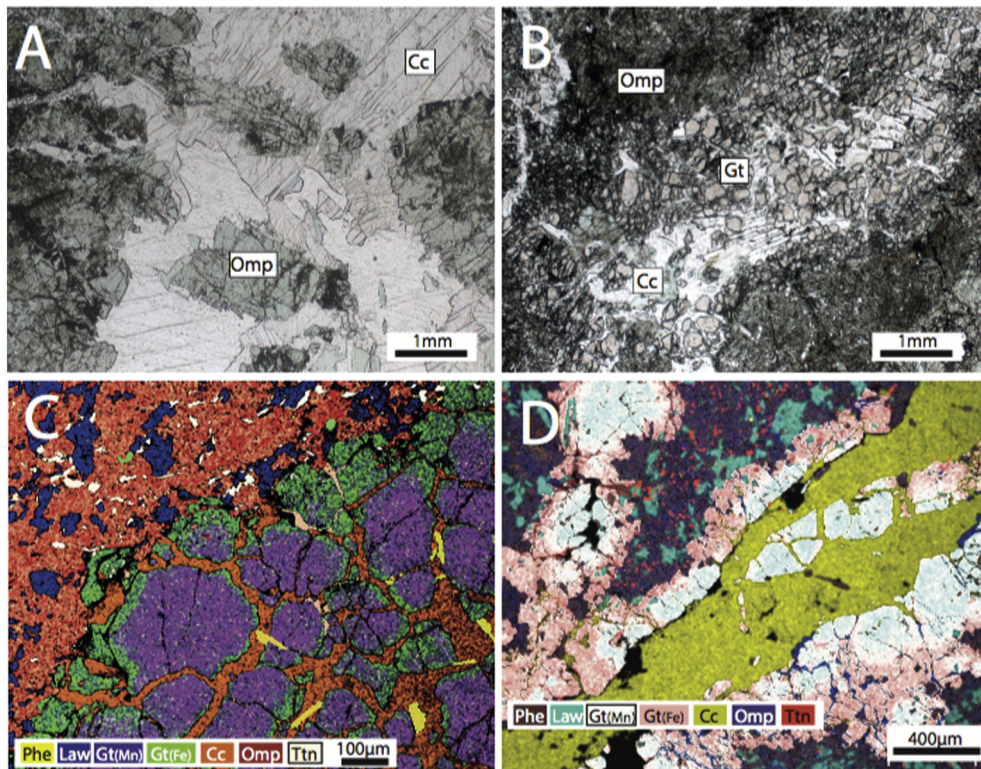
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The garnet composition resulting from reaction (4) between epidote and carbonate is enriched in grossular component [ $X_{\text{Grs}} = 0.87$ ;  $X_{\text{Alm}} = 0.13$ ], in contrast to the composition of Gt2 in the sample [ $X_{\text{Grs}} = 0.4$ ;  $X_{\text{Alm}} = 0.6$ ]. Taking the composition of Gt2 as a proxy, the garnet formation resulted from decomposition of the former minerals clinozoisite/epidote, aragonite, quartz, and additional Fe-Mg-Mn-bearing minerals (e.g., seafloor hydrothermal celadonite and/or Fe-oxyhydroxides; prograde chlorite, amphibole). It is worth noting that the reaction between hydrous silicate and carbonate ((1) and (2)) consumes a significant amount of quartz in the rock. These reactions could not take place in standard silica-undersaturated metabasalts, whereas they are favored in seafloor hydrothermal products containing free quartz as a reactant, as observed in the seafloor hydrothermal products preserved in the Corsica metabasalts (Figs. 3, 4C). Nevertheless, our data suggest that the size and initial mineral assemblage of the inherited hydrothermal veins controlled the extent of fluid channelization and magnitude of decarbonation reactions in the rock. As an example, Ep1-bearing large inherited veins in hollow pillow metabasalts (see Figs. 4C,D, 5A, 6B) show extensive decarbonation reactions, whereas Ep-1-free small, inherited cooling fractures in metapillow cores (see Figs. 4A,B, 5B, 6E) do not.

591



**Fig. 9.** Photomicrographs of sample OF3156 [inherited, randomly oriented carbonate veins (Group 1) from the San Petrone metabasalts]; PPL. (A) Carbonate vein crosscutting an undeformed, eclogite-facies metabasalt. Note the preservation of the primary igneous texture overgrown by dominant omphacite and lawsonite, and minor garnet. Along the vein, two large (ca. 2 mm) pseudo-hexagonal concentric structures are observed (cf. B for close up), and probably correspond to former aragonite basal sections now converted to calcite. (C) Example of lawsonite eclogite-facies re-equilibration in the inherited vein. Note the presence of garnet, zoned omphacite and lawsonite, the latter being concentrated at the vein wall (bottom-right).



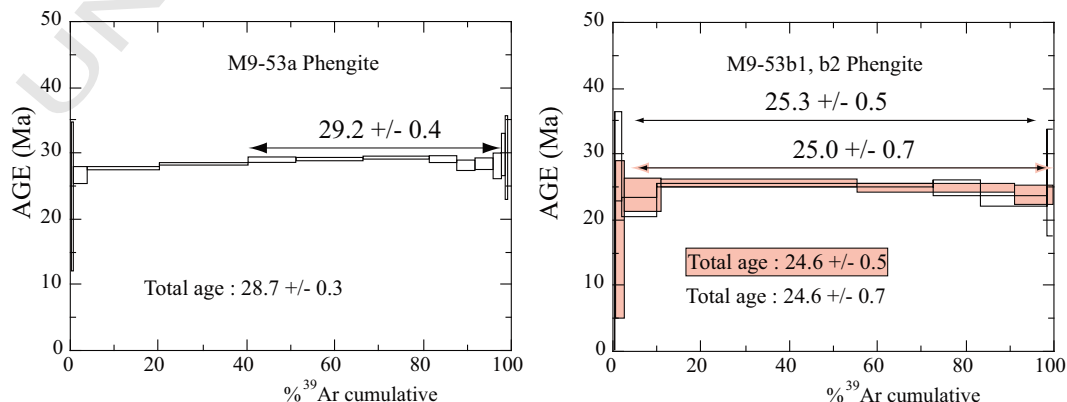
**Fig. 10.** Photomicrographs (PPL), BSE images and X-Ray composite compositional maps of carbonate-bearing metamorphic crack-seals. The selected example consists of a polyphase vein system including a first omphacite-garnet generation, followed by a second generation consisting of carbonate + phengite ± omphacite. In (A), the first generation assemblage is hydrofractured and sealed by the carbonate-rich assemblage. (B) Detail of a fractured omphacite vein sealed by carbonate. (C–D) Selvage of a composite vein crosscutting the host metabasalt (top-left). The effect of fracturing during carbonate and phengite precipitation is supported by the truncated zonation in the garnet. In (D), note the presence of two garnet veins cutting the host metabasalt (omphacite-lawsonite-titanite zones), only one of which was successively reworked during carbonate precipitation. Abbreviations as Fig. 8, plus Phe: phengite; Omp: omphacite; Ttn: titanite.

## 592 8. Fluid composition and time-integrated fluid flux

593 We conducted phase-equilibrium calculations to link the garnet  
594 forming reactions to decarbonation in the lithologic unit. Owing to the  
595 compositional and mineralogical microdomains, standard pseudosection  
596 modeling based on bulk-rock compositions cannot reflect local phase  
597 relations (e.g., Stüwe, 1997; Guevara & Caddick, 2016), especially for  
598 the low-temperature (<600 °C) assemblage. We therefore considered  
599 single or coupled reactions (1), (2) and (3) to solve local equilibria  
600 involving garnet formation in sample Lancone12-6.

601 We used the internally-consistent thermodynamic dataset of  
602 Holland and Powell (1998), a MATLAB-based code package to perform  
603 the thermodynamic calculations (Chu and Ague, 2013), and updated

activity models (garnet: White et al., 2007; epidote: Holland and  
604 Powell, 1998; H<sub>2</sub>O-CO<sub>2</sub>: Holland and Powell, 2003). The activities of  
605 garnet and epidote are calculated using the representative compositions  
606 in the prograde assemblage (Lancône12-6: Gt2 X<sub>Alm</sub> = 60; X<sub>Grs</sub> = 40;  
607 Ep1: X<sub>Ep</sub> = 16; X<sub>Zo</sub> = 84; Table 2). These calculations were done by  
608 considering previous estimates of the prograde P-T path for these  
609 rocks (Ravna et al., 2010; Vitale Brovarone et al., 2011b) and the T calcu-  
610 lated for the carbonate-garnet isotopic equilibrium. Additional details  
611 of thermodynamic calculation are provided in the Supplementary  
612 Material. P-T contours are calculated at specified fluid compositions  
613 (X<sub>CO<sub>2</sub></sub>) (reactions (1) and (2)) or oxygen fugacities (f<sub>O<sub>2</sub></sub>) (reaction (3))  
614 (Fig. 14). For reactions (1) and (2), the assemblage at higher T reaches  
615 equilibrium with a higher-X<sub>CO<sub>2</sub></sub> fluid. The assemblage epidote + garnet  
616



**Fig. 11.** Ar-Ar phengite plots for two samples of carbonate-bearing crack-seals.

t1.1 **Table 1**  
t1.2 Selected samples and analytical strategy.

t1.3	Sample	Group	Locality	Facies <sup>a</sup>	Peak T <sup>a</sup>	Peak P <sup>a</sup>	Petrography	Mineral chemistry	Thermodynamic modeling	Carbonate bulk $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$	Garnet in-situ $\delta^{18}\text{O}$	Phengite Ar-Ar
t1.4	2cor14-2	1	San Colombano	Sub-greenschist	300 °C	0.4 GPa	X	X				
t1.5	Cor16-62a	1	Bocca di Serna	Sub-greenschist	300 °C	0.4 GPa	X	X				
t1.6	Cor16-62b	2	Bocca di Serna	Sub-greenschist	300 °C	0.4 GPa	X	X				
t1.7	Lancône-pillow	1	Défilé de Lancône	Lawsonite-eclogite	450–500 °C	1.9–2.6 GPa	X	X		X	X	
t1.8	OF3156	1	San Petrone	Lawsonite-eclogite	500–540 °C	2.2–2.4 GPa	X	X				
t1.9	Lancône12-6	1	San Petrone	Lawsonite-eclogite	500–540 °C	2.2–2.4 GPa	X	X	X			
t1.10	OF3322	3	San Petrone	Lawsonite-eclogite	500–540 °C	2.2–2.4 GPa	X	X		X		X
t1.11	2COR12-8/M9-53a <sup>b</sup>	3	San Petrone	Lawsonite-eclogite	500–540 °C	2.2–2.4 GPa	X	X		X		X
t1.12	2COR12-11/M953b <sup>b</sup>	3	San Petrone	Lawsonite-eclogite	500–540 °C	2.2–2.4 GPa	X	X		X		X
t1.13	Acor14-16a,c	4	Défilé de Lancône	Lawsonite-eclogite	450–500 °C	1.9–2.6 GPa	X	X				

t1.14 <sup>a</sup> See text for references.

t1.15 <sup>b</sup> The two samples are equivalent.

617 is metastable on the high-pressure side of the lawsonite/epidote transi-  
618 tion. At the same P-T conditions, the meta-stable epidote-bearing  
619 assemblage is in equilibrium with a fluid of higher  $X_{\text{CO}_2}$  (dashed curves in  
620 Fig. 14) than the lawsonite-bearing assemblage (solid curves in  
621 Fig. 14). The  $f_{\text{O}_2}$  contours of reaction (3) are sensitive to pressure, as  
622 discussed by Donohue and Essene (2000) for equivalent redox reac-  
623 tions. The epidote and garnet of interest, if equilibrated at higher P,  
624 suggest more oxidized conditions than in a low-P assemblage.

625 In this calculation, we assume that the mineral assemblage recorded  
626 the equilibrium with the fluid at one specific P-T condition along the  
627 prograde path. Garnet in Alpine Corsica metabasalts is found uniquely  
628 in eclogite-facies rocks (Vitale Brovarone et al., 2014), and the T esti-  
629 mate ~500 °C obtained for the carbonate-garnet isotopic equilibrium is  
630 comparable with previous peak metamorphic conditions (~500 °C and  
631 2.2 GPa Ravna et al., 2010; Vitale Brovarone et al., 2011b). We thus  
632 reasonably assume that garnet formation in local (meta-) stable  
633 domains occurred at or close to peak P-T metamorphic conditions,  
634 where the fluid  $X_{\text{CO}_2}$  is about 0.2–0.4 mol%, with the  $f_{\text{O}_2}$  ~FMQ + 1. The  
635 estimated  $X_{\text{CO}_2}$  at the peak conditions is reasonably consistent with  
636 the  $\text{CaCO}_3$  solubility in water (~0.2 mol%, Caciagli and Manning, 2003).

637 When the fluid flows along a T and/or P gradient, the fluid changes  
638 its composition in response to the changes in P-T conditions, which re-  
639 flects the reaction progress. For the devolatilization reaction (1), when  
640 1 mol grossular is precipitated in the rock, 2 mol  $\text{CO}_2$  and 2 mol  $\text{H}_2\text{O}$   
641 are released to the fluid. For reaction (2), 1 mol grossular corresponds  
642 to 5/3 mol  $\text{CO}_2$  and 1/3 mol  $\text{H}_2\text{O}$ . Accordingly, if the devolatilization pro-  
643 cesses were taking place in a closed system,  $\text{CO}_2$  would be greatly  
644 enriched in the fluid with small reaction progress (Greenwood, 1975).  
645 However, if the fluid is in equilibrium with the garnet-forming matrix  
646 along the flow path, the time-integrated flux can be thus estimated  
647 based on fluid mass conservation (Baumgartner and Ferry, 1991; See  
648 Supplementary Material for details and discussions). Calculations are  
649 conducted to estimate the time-integrated fluid flux into the rock to  
650 drive the devolatilization reactions at any P-T condition along the pro-  
651 grade P-T path, assuming that fluid flow was predominantly vertically  
652 upward through the metabasalt unit.

653 The time-integrated fluid flux ( $\text{m}^3/\text{m}^2$ ) and  $\text{CO}_2$  flux ( $\text{g}/\text{m}^2$ ) cor-  
654 responding to garnet precipitation (1 g garnet per  $1 \text{ m}^3$  rock) are  
655 presented in Fig. 15. At P-T conditions close to the prograde path,  
656 1 g garnet ( $X_{\text{Grs}} = 0.4$ ) precipitates in  $1 \text{ m}^3$  rock in response to  
657  $0.01$ – $0.02 \text{ m}^3 \text{ H}_2\text{O-CO}_2$  fluid flowing through  $1 \text{ m}^2$  into the rock.  
658 The infiltrating fluid flux contains  $50$ – $70 \text{ g}/\text{m}^2 \text{ CO}_2$ , depending on  
659 the specific reactants and P-T conditions. We do not imply that the  
660 mineral assemblages were in equilibrium with the fluid throughout  
661 the prograde metamorphism, but the flux expression above depends  
662 on the fluid compositional gradient rather than the absolute values.  
663 The simulations by Ague (1998) demonstrate that even in disequilib-  
664 rium, compositional gradients approach the local equilibrium case  
665 along the majority of the flow path, so the flux estimates based on

equilibrium assumption are still valid. We also note that the different  
P-T conditions do not cause order-of-magnitude differences in the  
fluid flux estimates.

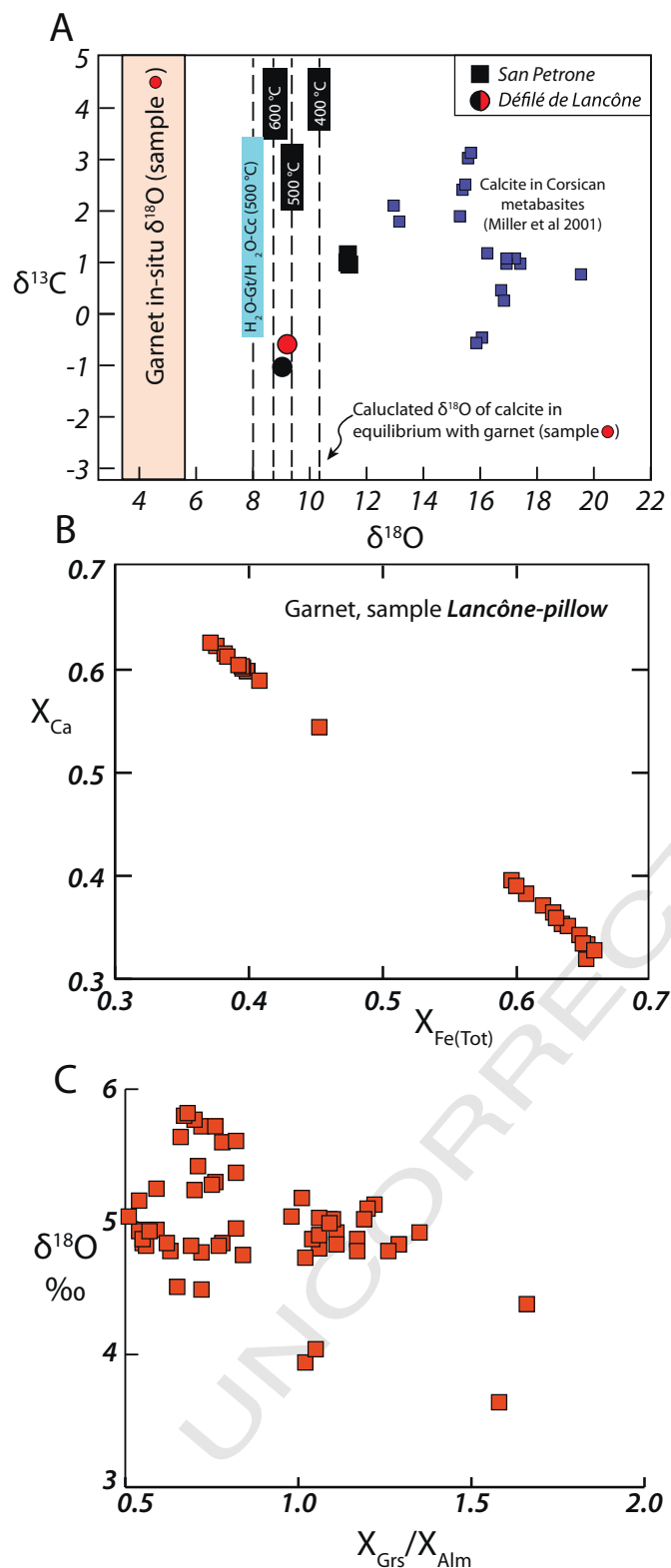
666 If the preserved mineral compositions reflect the peak stage then,  
667 for instance, 1 g garnet product in  $1 \text{ m}^3$  rock by local devolatilization  
668 reactions corresponds to about  $0.01 \text{ m}^3/\text{m}^2$  fluid flux flowing through  
669 (including  $\sim 70 \text{ g}/\text{m}^2 \text{ CO}_2$ ). The fluid flux is a cumulative effect of  
670 devolatilization of the whole subduction section, so it is much larger  
671 than that generated from local devolatilization reactions where garnets  
672 are formed.

673 The garnet amount in our samples reaches ~20 vol%. We estimate  
674 that the garnet amount produced by the reactions between carbonates,  
675 epidote/lawsonite and quartz accounts for at least 40% of total garnet  
676 (8 vol% taking 20 vol% garnet in the rock; taking Gt2 and reaction (2)  
677 as a proxy for garnet). Moreover, the remaining 12 vol% is much  
678 larger than the garnet mode in the carbonate-free metabasalts, so it  
679 is highly likely that several other carbonate-consuming reactions  
680 took place in the rock. Taking 8 and 20 vol% garnet to correspond  
681 to  $3 \times 10^5$  and  $7.6 \times 10^5 \text{ g}$  per  $1 \text{ m}^3$  rock, respectively, yields upper  
682 and lower limits of the estimate of the fluid flux through the rock  
683 of  $3 \times 10^3$  and  $7.6 \times 10^3 \text{ m}^3/\text{m}^2$ . These values are in agreement  
684 with estimated time integrated fluid fluxes in crustal metamorphic  
685 settings, and plot transitionally between flux ranges typically recog-  
686 nized in dominantly pervasive ( $<10^3 \text{ m}^3/\text{m}^2$ ) and highly channel-  
687 ized ( $>10^4 \text{ m}^3/\text{m}^2$ ) flow systems (Ague, 2014). The values are,  
688 however, much higher than the time-integrated fluid flux proposed  
689 at the top of an oceanic slab for a vertical flow ( $3 \times 10^2 \text{ m}^3/\text{m}^2$ ;  
690 Zack and John, 2007). The time-integrated fluid flux leading to the  
691 garnet precipitation carried a  $\text{CO}_2$  flux as high as 20–50  $\text{t}/\text{m}^2$ .

## 9. Discussion

### 9.1. Origin and significance of the carbonated metabasalts of Alpine Corsica

692 Considerable effort has been made to estimate the amount of car-  
693 bonate incorporated in oceanic basalts and its role as a carrier of C  
694 into active subduction (Staudigel et al., 1996; Jarrard, 2003; Staudigel,  
695 2003). The study of metamorphic rocks formed tens of Ma ago (i.e. in  
696 the Jurassic for the Corsica samples) also requires consideration of  
697 long-term variation over geological timescales (Jarrard, 2003). Gillis  
698 and Coogan (2011) reviewed data from seven DSDP/ODP drill cores,  
699 and concluded that the carbonate content of the upper 300 m of the vol-  
700 canic crust is higher in the slower-spreading Atlantic (0.8–4.2 wt%) than  
701 in the Pacific (0.2–2.6 wt%) crust. In both settings, the Mesozoic crusts  
702 are 2 to 13 times richer in carbonate than the Cenozoic ones (Gillis  
703 and Coogan, 2011). The Corsican basalts originated in a Mesozoic,  
704 Tethyan ocean-continent transition zone characterized by an overall  
705 crustal architecture typical of slow-spreading oceans (Lagabrielle  
706 and Lemoine, 1997; Lagabrielle et al., 2015). Therefore, in terms of C  
707 710 711



**Fig. 12.** (A) Diagram summarizing the whole rock carbonate ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and in-situ garnet ( $\delta^{18}\text{O}$ ) stable isotope data. Previous data on eclogite-facies metabasites from Corsica are also reported (after Miller et al., 2001). The calculated  $\delta^{18}\text{O}$  of calcite in equilibrium with the measured garnet values are also reported for 400, 500 and 600 °C, as well as the calculated value of  $\text{H}_2\text{O}$  in equilibrium with the measured garnet and carbonate values at 500 °C. (B) Diagram showing the bimodal zonation of Gt2 in sample Lancône-pillow alternating Ca-rich and Ca-poor zones. (C) Plot illustrating the slight inverse correlation between the Ca content in the garnet and the relative in-situ  $\delta^{18}\text{O}$  values by SIMS.

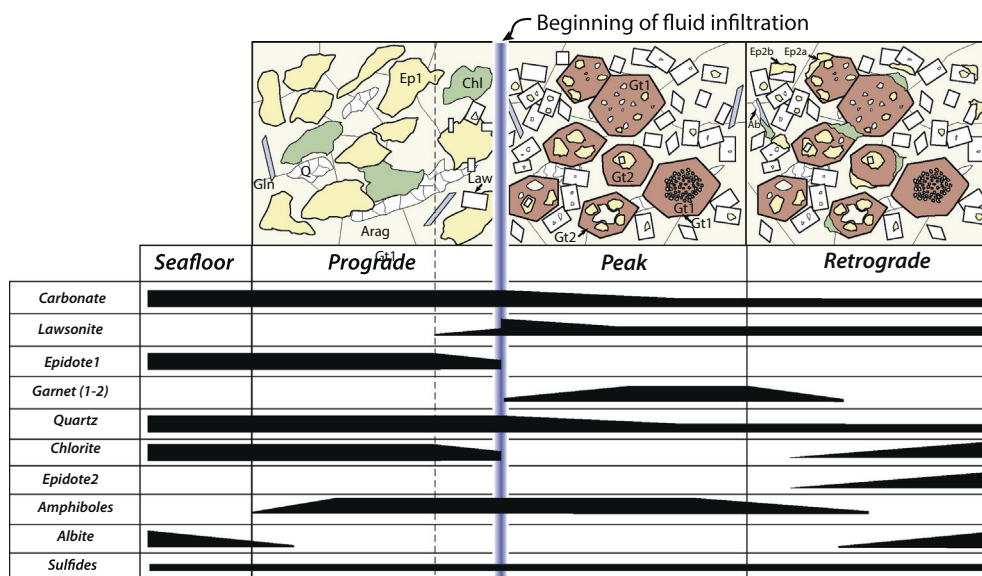
content, the Corsica metabasalts can be considered as a carbonate-rich end-member. 712

Carbonate in oceanic basalts is mainly found in hydrothermal veins, 714 or as disseminated material filling vesicles and intergranular void space 715 (Alt, 1995; Alt and Teagle, 1999). Carbonate precipitation most commonly 716 occurs in relatively LT hydrothermal veins (<100 °C). A notable 717 exception is Hole 504B, where carbonate formed at T up to 250 °C 718 (Alt et al., 1986; Alt and Teagle, 1999). Carbonate (dominantly calcite 719 and minor aragonite) can also replace olivine, simultaneously precipi- 720 tating phyllosilicates (e.g. saponite, celadonite) and Fe-oxyhydroxides. 721 Carbonate is rarely found in association with epidote, the latter being 722 formed at higher T together with quartz. Nonetheless, HT carbonate, 723 epidote and quartz is found in Hole 504B, together with stockwork 724 sulfide deposits. Most Corsican basalts (both weakly metamorphosed 725 basalts and HP metabasalts) preserve seafloor hydrothermal veins 726 showing little or no Alpine deformation. Some of these veins have 727 features characteristic of low-T seafloor carbonate precipitation 728 (carbonate, phyllosilicates; Fig. 4a) and their metamorphic transforma- 729 tions (Fig. 4B), whereas others preserve evidence for high-T seafloor 730 hydrothermal alteration (Fig. 4C) similar to Hole 504B, such as high 731 epidote (Ep1), quartz, carbonate, and sulfide abundances and their 732 metamorphic transformations (Fig. 4D). 733

## 9.2. Evidence for open-system behavior at eclogite-facies conditions and infiltration of aqueous fluids 734 735

Our rocks do not show macroscopic evidence for fluid influx, e.g. 736 outcrop-scale metasomatic halos. Despite that, the petrological observa- 737 tions suggest infiltration of external fluids during garnet formation 738 during the prograde evolution. The available P-T estimates on the HP 739 units of Alpine Corsica indicate that the prograde P-T path lies in the 740 lawsonite stability field, where epidote should not be stable. Neverthe- 741 less, relict prograde epidote (Ep1) is widespread in our samples. Our 742 microstructural study indicates that the conversion from Ep1 to 743 lawsonite occurred during, or slightly before, garnet formation at 744 eclogite-facies conditions (Fig. 13). For example, lawsonite replacing 745 Ep1 is found as inclusions in garnet. Three main scenarios can account 746 for the presence of epidote during the prograde evolution of our sam- 747 ples, (i) the presence of a high  $X_{\text{CO}_2}$  fluid composition (Nitsch, 1972), 748 (ii) insufficient water content (Ballèvre et al., 2003), and/or (iii) meta- 749 stable preservation of seafloor hydrothermal epidote. The first hypoth- 750 esis is unlikely in our case because titanite, which is even more 751 sensitive to the  $X_{\text{CO}_2}$  than lawsonite, was stable throughout the 752 prograde evolution instead of rutile, as indicated by widespread titanite 753 inclusions in garnet. The second hypothesis requires that the system 754 was initially water-undersaturated, and the prograde, near-peak forma- 755 tion of lawsonite at the expense of Ep1 would therefore require signifi- 756 cant hydration during the prograde path (Ballèvre et al., 2003; Clarke 757 et al., 2006; Groppo et al., 2016). The third hypothesis (metastable pres- 758 ervation of epidote) requires overstepping of the expected lawsonite- 759 forming reactions during the prograde path. This is not uncommon 760 for such kinds of hydration reactions, which are expected to have low 761 reaction affinity at low temperatures (Pattison et al., 2011; Ague and 762 Carlson, 2013). Successive conversion of metastable epidote to 763 lawsonite would require significant addition of water to the system, 764 a process that is also expected to significantly lower the degree 765 of overstepping (Pattison et al., 2011). Therefore, hypothesis (iii) also 766 indirectly supports a fluid influx for the precipitation of lawsonite 767 (hypothesis ii). This indicates that the prograde conversion of epidote 768 to lawsonite resulted from hydration of undersaturated metabasalts at 769 HP conditions, as already documented in fluid-mediated systems in 770 Corsica and other HP belts and predicted by numerical models (Wada 771 et al., 2012; Faccenda, 2014; Vitale Brovarone and Beysac, 2014; 772 Groppo et al., 2016). Interestingly, part of this newly formed lawsonite 773 was then destabilized, with related water release, during decarbonation 774 and garnet formation (reaction (1)) (Fig. 13). This demonstrates the 775





**Fig. 13.** Petrological evolution of sample Lancône12-6 reconstructed based on textural data. This sample shows well the complexity and diversity of the local mineral assemblages and equilibria in the studied rocks. Note that the beginning of fluid infiltration, recorded by hydration and conversion of Epidote1 to lawsonite, is followed by coupled dehydration and decarbonation processes, suggested by the consumption of lawsonite, Epidote1, carbonate and quartz to produce garnet. Abbreviations as Fig. 8.

776 complex role of fluid infiltration in the coupling between hydration  
 777 and dehydration/decarbonation processes during the metamorphic  
 778 evolution of subducting slabs.

779 *9.3. Carbon and oxygen isotopic fingerprints of metamorphic decarbonation*

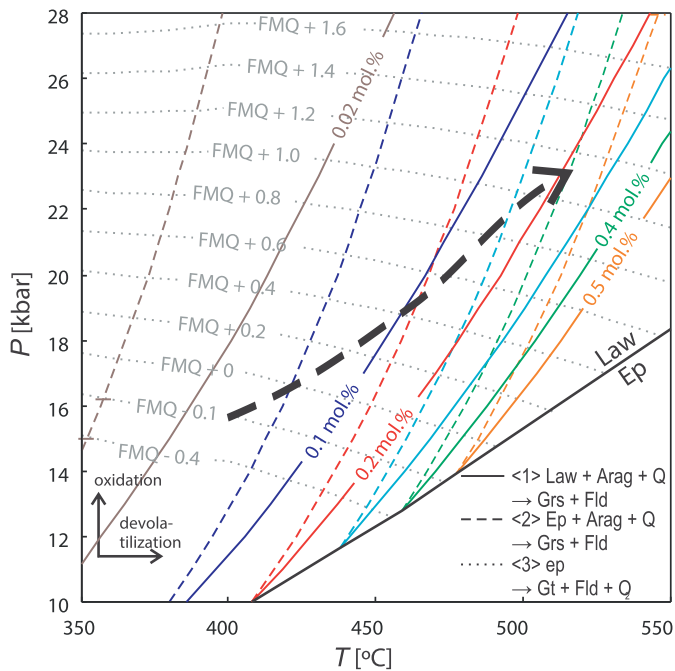
780 Variations in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for carbonate in metamorphic  
 781 rocks are used as markers for decarbonation processes in subduction  
 782 zones. For example, Cook-Kollars et al. (2014) and Miller et al. (2000,  
 783 2001) provided large datasets on C and O isotopic data on carbonate-  
 784 bearing rocks from the Western Alps and Alpine Corsica. Both studies  
 785 noticed little shift in  $\delta^{13}\text{C}$  relative to the inferred marine signature

(‰), and interpreted these values as slightly affected by decarbonation  
 786 or fluid-rock interactions. Nevertheless, eclogite-facies rocks affected by  
 787 intense carbonate dissolution in the Syros mélangé (Greece) show very  
 788 little decrease in  $\delta^{13}\text{C}$  relative to unaltered rocks (Ague and Nicolescu,  
 789 2014), indicating that the interpretation of  $\delta^{13}\text{C}$  values of subducted  
 790 carbonates in open systems requires caution. In our samples, although  
 791 several mineralogical and textural pieces of evidence indicate that  
 792 decarbonation reactions occurred during subduction, the carbonate  
 793  $\delta^{13}\text{C}$  values do not show significant shifts relative to a reference marine  
 794 carbonate source (Fig. 12A).  
 795

Our calculations show that a fairly large amount of C-bearing fluid  
 796 passed through our rock to drive the inferred decarbonation reactions  
 797

t2.1 **Table 2.**

	Lancône-pillow		Lancône12-6		Lancône12-6			Lancône12-6		Lancône12-6		OF3322					
	Gt2	Gt2	Gt1	Gt2	Ep1	Ep2	Ep2	Blue-Amp	Green-Amp	Chl	Phe	Phe					
	Dark	Bright				after Gt	after Law										
t2.5	SiO <sub>2</sub>	37.67	36.67	37.63	38.28	SiO <sub>2</sub>	38.52	38.66	40.38	SiO <sub>2</sub>	57.53	57.12	SiO <sub>2</sub>	26.83	SiO <sub>2</sub>	53.47	53.64
t2.6	Al <sub>2</sub> O <sub>3</sub>	18.57	20.64	21.03	20.76	Al <sub>2</sub> O <sub>3</sub>	27.78	26.94	30.89	Al <sub>2</sub> O <sub>3</sub>	10.54	7.96	Al <sub>2</sub> O <sub>3</sub>	19.83	Al <sub>2</sub> O <sub>3</sub>	23.43	23.12
t2.7	TiO <sub>2</sub>	0.01	0.11	0.12	0.18	MgO	0.02	0.00	0.02	TiO <sub>2</sub>	0.00	0.10	MgO	23.34	TiO <sub>2</sub>	0.07	0.13
t2.8	MgO	18.49	30.07	29.20	26.40	FeO	7.38	8.14	3.34	MgO	12.85	11.91	FeO	0.29	MgO	2.99	3.07
t2.9	FeO	0.06	0.52	0.54	0.44	MnO	0.11	0.03	0.24	FeO	0.00	0.14	MnO	16.77	FeO	0.02	0.02
t2.10	MnO	0.00	0.07	0.53	0.39	CaO	23.57	23.58	23.24	MnO	8.83	11.31	CaO	0.06	MnO	4.64	4.68
t2.11	CaO	23.95	11.69	11.38	14.08	Na <sub>2</sub> O	0.09	0.02	0.21	CaO	0.92	4.49	Na <sub>2</sub> O	0.10	CaO	0.06	0.05
t2.12	Na <sub>2</sub> O	0.00	0.00	0.04	0.03	K <sub>2</sub> O	0.03	0.00	0.01	Na <sub>2</sub> O	6.93	5.18	K <sub>2</sub> O	0.03	Na <sub>2</sub> O	0.12	0.09
t2.13	K <sub>2</sub> O	0.00	0.01	0.00	0.01	Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	K <sub>2</sub> O	0.00	0.04	Cr <sub>2</sub> O <sub>3</sub>	0.00	K <sub>2</sub> O	10.63	10.78
t2.14	Cr <sub>2</sub> O <sub>3</sub>	0.00	0.04	0.00	0.02	Total	97.51	97.39	98.35	Cr <sub>2</sub> O <sub>3</sub>	0.07	0.00	Total	87.24	Total	95.43	95.59
t2.15	Total	98.75	99.81	100.47	100.58					Total	97.66	98.25					
t2.16						Si	2.99	3.01	3.06				Si	5.61	Si	3.57	3.58
t2.17	Si	3.00	2.96	3.00	3.03	Ti	0.00	0.00	0.00	Si	7.96	7.94	Al iv	2.39	Ti	0.00	0.01
t2.18	Al iv	0.00	0.04	0.00	0.00	Al	2.55	2.47	2.76	Al iv	0.04	0.06	Al vi	2.51	Al	1.84	1.82
t2.19	Al vi	1.76	1.93	1.98	1.94	Cr	0.00	0.00	0.00	Al vi	1.68	1.24	Cr	0.00	Fe <sup>3+</sup>	0.00	0.00
t2.20	Ti	0.00	0.01	0.01	0.01	Fe <sup>3+</sup>	0.48	0.53	0.21	Ti	0.00	0.01	Fe <sup>3+</sup>	0.04	Fe <sup>2+</sup>	0.17	0.17
t2.21	Cr	0.00	0.00	0.00	0.00	Mn	0.01	0.00	0.02	Cr	0.01	0.00	Fe <sup>2+</sup>	4.04	Mn	0.00	0.00
t2.22	Fe <sup>3+</sup>	0.21	0.05	0.02	0.02	Mg	0.00	0.00	0.00	Fe <sup>3+</sup>	0.21	0.05	Mn	0.05	Mg	0.46	0.47
t2.23	Fe <sup>2+</sup>	1.02	1.98	1.93	1.72	Ca	1.96	1.97	1.89	Fe <sup>2+</sup>	1.27	1.33	Mg	5.23	Ca	0.00	0.00
t2.24	Mn	0.00	0.04	0.04	0.03	Na	0.00	0.00	0.03	Mn	0.00	0.02	Ca	0.01	Na	0.02	0.01
t2.25	Mg	0.00	0.01	0.06	0.05	K	0.00	0.00	0.00	Mg	1.82	2.34	Na	0.08	K	0.90	0.92
t2.26	Ca	2.04	1.01	0.97	1.19	Total	7.99	7.99	7.97	Ca	0.14	0.67	K	0.02			
t2.27	Total	9.27	8.03	8.00	7.99	XEp	0.2	0.2	0.1	Na	1.86	1.40	Oxygens	28			
t2.28	XCa	0.62	0.33	0.32	0.40					K	0.00	0.01	XMg	0.56			
t2.29	XMg	0.00	0.00	0.02	0.02					Oxygens	23	23					
t2.30	XFe	0.38	0.66	0.65	0.58												
t Q5	XMn	0.00	0.01	0.01	0.01												



**Fig. 14.** Diagram illustrating the stable or metastable equilibria among lawsonite, epidote and garnet at specific  $X_{\text{CO}_2}$  (mol%) and  $f_{\text{O}_2}$  (relative to the FMQ buffer) in the lawsonite-bearing zone. The prograde path is superimposed for reference (after Vitale Brovarone et al., 2011a). Abbreviations: Law: lawsonite; Arag: aragonite; Q: quartz; Grs: grossular; Ep: epidote; Gt: garnet; Fld: fluid. See text for details.

Q4

( $>20 \text{ t/m}^2$  of  $\text{CO}_2$ ), suggesting that the isotopic composition of C in this fluid may have contributed to the final  $\delta^{13}\text{C}$  composition of residual carbonate. If the incoming fluid was derived from dissolution of marine carbonate following the patterns observed by Ague and Nicolescu (2014), the final  $\delta^{13}\text{C}$  values of the residual carbonate would not have changed significantly in the studied rocks. The  $\delta^{13}\text{C}$  values of carbonate in the metamorphic crack-seals are consistent with transport of carbon preserving marine isotopic signatures. In sum, we conclude that the absence of significant shifts in  $\delta^{13}\text{C}$  values does not necessarily imply that little decarbonation occurred.

The  $\delta^{18}\text{O}$  values (9–11‰) of carbonate in the selected set of samples are lower than the average composition of carbonate in the Corsican metaophiolite 12–20‰, Miller et al., 2001 (Fig. 12C). Miller et al. (2001) interpreted the average values in the HP metabasaltic rocks of Corsica as evidence for the absence of large-scale, pervasive fluid flow and isotopic homogenization of the subducted altered oceanic crust. Conversely, our samples testify for isotopic equilibration at near peak conditions (see Section 6). This feature further suggests that the selected set of samples recorded channelized fluid flow enhancing isotopic equilibration of marine carbonates with silicates in the metabasaltic rocks at HP conditions. The collected in-situ  $\delta^{18}\text{O}$  garnet data may constrain the timing and conditions for this equilibration. Ca-silicates resulting from decarbonation reactions in our samples are expected to inherit at least part of the  $\delta^{18}\text{O}$  of the precursor carbonate, unless the rock  $\delta^{18}\text{O}$  is buffered by the signature of the incoming fluid. However, if the reactant carbonate and/or the incoming fluid are equilibrated with the metabasaltic host rocks, the decarbonation reaction may not be obviously deduced by the  $\delta^{18}\text{O}$  signature. The  $\delta^{18}\text{O}$  values of

t3.1 **Table 3**

t3.2		d13C PDB	d18O SMOW
t3.3	2COR12-11	1.0	11.4
t3.4	OF3322	1.2	11.4
t3.5	2COR12-8	1.0	11.4
t Q6	Lancône-pillow	−0.6	9.1

Ca-rich garnet formed through decarbonation reactions do not show any significant shift relative to the Ca-poorer garnet (Fig. 13B). The absence of significant  $\delta^{18}\text{O}$  variations between the garnet generations suggests that the system was buffered by an external fluid source rather than by local “closed” equilibria. The latter hypothesis would suggest that the infiltrating fluid had a  $\delta^{18}\text{O}$  signature equilibrated with the metabasaltic sequence (6–11‰) in the Défilé de Lancône, (Miller et al., 2001). The  $\delta^{18}\text{O}$  composition of carbonate in the metamorphic veins (about 11‰) supports this hypothesis.

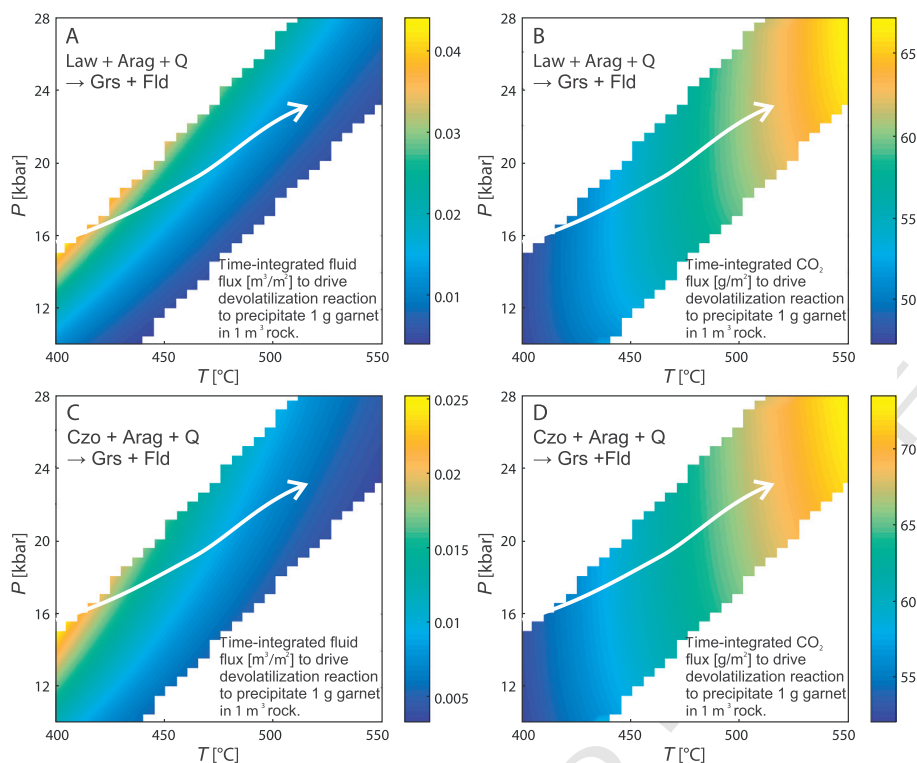
#### 9.4. Role of inherited seafloor hydrothermal structures on devolatilization and C circulation in subduction zones

The modes of carbonation and the spatial distribution of carbonate in the rock require additional discussion. Carbonate incorporation in the oceanic crust can be strongly inhomogeneous and localized (see Section 9.1). Owing to the complexity and variability of alteration patterns, global budgets do not account for the spatial distribution of the carbonates at the meso and microscale. Most thermodynamic studies investigating the general decarbonation patterns of oceanic subduction consider averaged oceanic basalt compositions (e.g. “Supercomposite” bulk composition of Staudigel et al., 1989) that cannot reproduce this variability. The choice of using an average composition is valid in the case of decarbonation reactions that do not directly correlate to the amount of carbonate in the rock, but may result in significant underestimations of the total produced C fluxes if carbonate dissolution is also relevant. As an example, decarbonation can be limited in carbonate-rich systems poor in silicates (Kerrick and Connolly, 2001; Gorman et al., 2006; Cook-Kollars et al., 2014). Carbonate-rich, silicate-poor hydrothermal veins may undergo little decarbonation compared to mixed carbonate-silicate assemblages, as also suggested by our data; conversely, fluid channelization along veins may potentially cause total carbonate dissolution (Ague and Nicolescu, 2014). Therefore, inherited hydrothermal systems may exert a chemical/structural feedback on C release in subduction zones.

The collected data show that large-scale chemical homogenization of subducted oceanic metabasalts is not necessarily achieved at forearc depths (see also conclusions by Miller et al., 2001), thus preserving localized domains containing carbonate amounts several times higher than the averaged compositions of altered oceanic basalts. This preservation is not only characteristic of the lawsonite-eclogites of Corsica, but is also observed in the blueschist- and eclogite-facies rocks from the Western Alps and other orogenic belts (Collins et al., 2015). Therefore, our samples can provide important insights on the potential role of structural inheritance on the patterns of C loss from subducted metabasalts.

Inherited hydrothermal vein networks are structures that may favor fluid channelization and fluid-rock interactions during subduction, as summarized in Fig. 16. The studied samples from Corsica provide the first natural evidence for such an effect, as demonstrated by the documented fluid-mediated isotopic reset, the coupled hydration-decarbonation reactions, and the estimated time-integrated fluid fluxes testifying for channelized fluid flow (see Section 8).

The composition (mineralogical and chemical) of the inherited hydrothermal material also plays an important role on the patterns of C release during subduction. The particular Ca-Al-Si-C-rich (and Fe-Mg poor) compositions (high initial carbonate, epidote, quartz) of the inherited hydrothermal veins may also be an important factor favoring decarbonation reactions that have been shown to be hampered in standard metabasaltic compositions where carbonate phases other than Ca carbonate are present (Kerrick and Connolly, 2001; Poli et al., 2009). The Fe-Mg-poor assemblages of the Corsica rocks play a key role in the development of the proposed decarbonation reactions. These particular bulk-rock compositions (together with other parameters such as  $f_{\text{O}_2}$ ) are probably responsible for the absence of Mg-Fe carbonates in our high-pressure assemblages, and may also have a

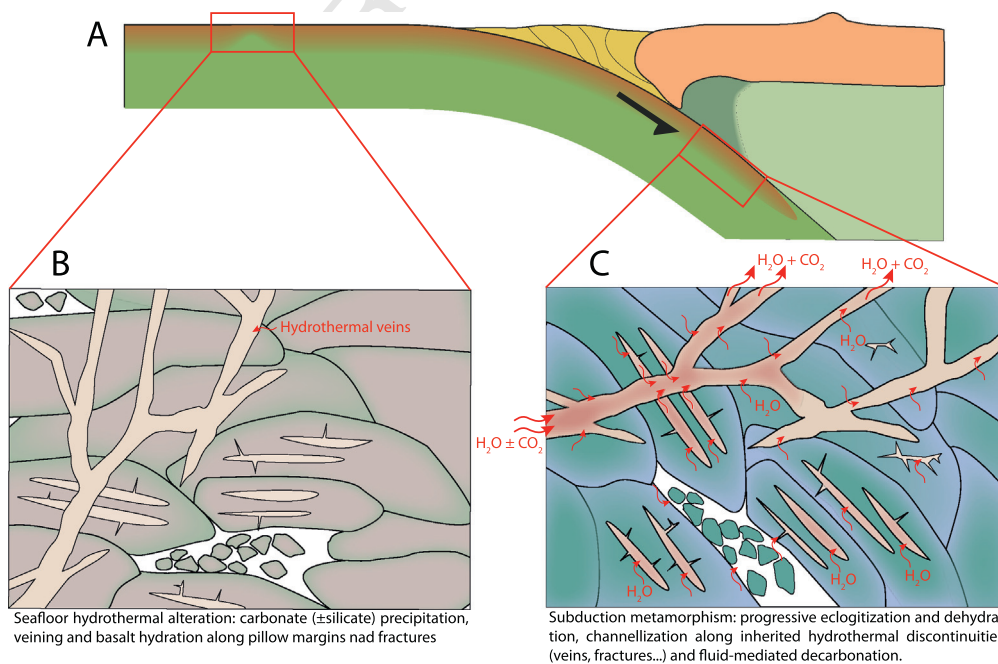


**Fig. 15.** Calculated time-integrated fluid flux ( $\text{m}^3/\text{m}^2$ , A, C) and  $\text{CO}_2$  flux ( $\text{g}/\text{m}^2$ , B, D) to precipitate 1 g garnet by devolatilization reactions between aragonite, quartz and lawsonite (reaction (1), A, B) or epidote (reaction (2), C, D). The prograde path is superimposed for reference (after Vitale Brovarone et al., 2011a). Abbreviations as Fig. 14.

890 potential role in generating Ca-rich carbonic melts at higher P-T condi- 897  
891 tions (Poli et al., 2009; Li et al., 2014; Poli, 2015).

892 Moreover, the chemical/mineralogical composition of these veins 898  
893 may exert a positive feedback on permeability, fluid channelization 899  
894 and decarbonation. Wark and Watson (2002) demonstrated experi- 900  
895 mentally that the mineral assemblage strongly controls grain-scale 901  
896 pore channelization in systems controlled by T or compositional 902

903 gradients. They showed that calcite-quartz-wollastonite rock is much 897  
904 more suitable for channelization than rock composed of calcite alone. 898  
905 This channelization effect is also documented in natural HP fluid- 899  
906 mediated systems (Molina et al., 2004). Nevertheless, in our rocks, 900  
907 decarbonation is particularly efficient in inherited hydrothermal 901  
908 veins containing initial carbonate, quartz and epidote, whereas it 902  
909 seems to be less marked in veins consisting dominantly of carbonate 903



**Fig. 16.** (A) Schematic representation of an oceanic subduction setting showing the position of basalts emplaced and hydrothermally altered at the ridge (B) and then successively subducted to high-pressure conditions (C). The scheme is not intended to fully represent the Corsica case study, but to help the reader following the structural inheritance from (B) to (C), and its role on fluid channelization and fluid-mediated decarbonation of oceanic hydrothermal carbonates during eclogitization and dehydration at high-pressure conditions.

(Supplementary material). This may be due to the interplay between mineralogical/permeability factors (Wark and Watson, 2002), even though this effect can be hampered by the progression of the decarbonation reactions (Balashov and Yardley, 1998). Last, fluid channelization along inherited hydrothermal systems can mobilize elements hosted in typical oceanic hydrothermal deposits, such as S and metals. Although our study did not focus on these elements, the studied samples contain possible evidence for transformation of sulfide deposits in the subducted metabasaltic suite (Figs. 4D, 6C).

### 9.5. Implications for deep C fluxes at subduction zones

Our study reports the first example of decarbonation reactions driven by fluid infiltration in a subducted segment of oceanic crust. The overall setting and field relations are consistent with the model of simple vertical fluid flow. Considering a standard geothermal model for the Corsica subduction (T increasing from the inner slab towards the overlying mantle wedge), this setting corresponds to decarbonation driven by an upward, up-T fluid flow. The cumulative time-integrated fluid flux passing through the rock and leading to the garnet precipitation carried a CO<sub>2</sub> flux as high as 20–50 t/m<sup>2</sup> (0.5–1.1 Mmol/m<sup>2</sup>). For comparison, decarbonation induced by the interaction between this fluid and the carbonate-bearing metabasalts would release 20–60 kg CO<sub>2</sub> from 1 m<sup>3</sup> rock considering reaction (1) or (2). The lower limit is close to the infiltration-driven decarbonation model of Gorman et al. (2006) (~0.5 wt% CO<sub>2</sub>, corresponding to 17 kg CO<sub>2</sub> from 1 m<sup>3</sup> rock).

In the Corsican slab, the basaltic section was thinner than 500 m, as indicated by lithostratigraphic observations in both low-grade units and their higher-grade equivalents (Miller et al., 2001; Vitale Brovarone et al., 2011a); a column of 500 m of such rock only releases 10–30 t/m<sup>2</sup> CO<sub>2</sub>. The deficiency of CO<sub>2</sub> flux suggests that the majority of CO<sub>2</sub> flux must be derived from deeper units of the subducting slab. The studied sequence consists of basal serpentinites (±metagabbro pods), metabasalts and metasedimentary cover rocks. Although the metasedimentary cover is locally thick (>200 m) in this sequence, previous tectonostratigraphic reconstructions suggest that the polarity of the studied unit was upright during subduction and was only later affected by large-scale folding and overturning during exhumation (Vitale Brovarone et al., 2013). Therefore, it can be assumed that the primary cover of this piece of subducted oceanic lithosphere did not contribute to these fluxes, and that the extra fluxes infiltrating the metabasaltic sequence were mainly contributed by the underlying serpentinites, in line with the measured garnet and carbonate isotopic signature. Alternatively, or in addition, if the documented fluid-rock interactions occurred after the detachment of the eclogite units along the plate interface, any other underlying subducting rocks (metasediments, metaigneous, serpentinites) may have contributed to these fluxes.

The peak pressure (2.2–2.3 GPa) roughly corresponds to the forearc depth of the fluid flux pulse from the subducting slab (Gorman et al., 2006). We compare our results with those predicted by the model of Gorman et al. (2006) at the same depths. For that, we calculated a hypothetical subduction rate for Corsica by using the available constraints on the age of blueschist-facies (37 Ma; 1.8 GPa) and eclogite-facies (34 Ma; 2.3 GPa) metamorphism (Martin et al., 2011; Vitale Brovarone and Herwartz, 2013). Taking a hypothetical dip of 45°, this gives subduction rates on the order of 0.7–0.8 cm/yr. These values are similar to the estimates for the HP units of the Western Alps (>0.7 cm/yr) (Rubatto et al., 1999). Assuming an ultra-slow subduction rate 0.8 cm/yr, the time-integrated CO<sub>2</sub> flux can be converted to 4–9 Mmol/yr per kilometer of arc length. These values are comparable to the cumulative predictions from phase equilibria analysis for cool subduction zones by Gorman et al. (2006) (≤3 Mmol/yr for the distillation decarbonation model and ≤13 Mmol/yr for the infiltration decarbonation model). However, we note that the thickness of metabasalt in the Corsican slab (≤500 m) is thinner than the model in Gorman et al. (2006) (2 km). Moreover, the carbonate-bearing marine sediment contributes more than half of the

cumulative carbon flux in Gorman et al.'s (2006) infiltration model, but such a layer is commonly thin or absent on the top of Corsica units. Thus, the general model of Gorman et al. (2006) cannot be directly applied to the Corsican study. If the contributions from the marine sediments and more than half of the metabasalt are removed from Gorman et al.'s (2006) model, the predicted cumulative time-integrated fluid flux would be significantly smaller in the infiltration decarbonation model. Thus, the order-of-magnitude estimates from natural observations in this study indicate that the decarbonation process in the subducting slab could be more intense than predicted by the conventional model. In addition to the decarbonation reactions in the basalt-sediment units (Gorman et al. 2006), other sources like the underlying mafic-ultramafic units and/or underlying subducting rocks, and other mechanisms including carbonate dissolution account for a large proportion of the total CO<sub>2</sub> fluxes from the slab.

### 9.6. Fate and residence time of carbonate in the fluid

Our data and estimates indicate that a large amount of carbonate-bearing fluid flowed during eclogite-facies metamorphism of Alpine Corsica. A proportion of these fluids may have reprecipitated carbonate minerals and other minerals at HP conditions (Piccoli et al., 2016) or have been consumed in retrograde reactions, whereas the rest was ultimately released to shallower reservoirs (Kelemen and Manning, 2015). The carbonate-bearing metamorphic crack-seals represent direct evidence for the reprecipitation of C-bearing fluids at HP conditions. The Ar-Ar dates of phengite from the carbonate-bearing eclogitic crack-seals yield minimum ages of about 29 Ma for this precipitation. This age is about 5 Ma younger than the eclogite-facies metamorphic peak for these rocks (34 Ma). Interestingly, eclogite veins from New Caledonia have been recently shown to have formed about 6 Ma later than the regional peak metamorphic conditions, and under very fast precipitation conditions (Taetz et al., 2018). These similar patterns suggest similar subduction/exhumation rates for the two fossil subduction systems and a common mechanism of fluid circulation and vein formation during the early decompression history of HP rocks. Furthermore, one of the two Corsica samples yields much younger ages of about 25 Ma (about 9 Ma younger than the age of peak metamorphism). This suggests that the C-bearing fluid remained within the slab for a long time span, although the peak metamorphic T of the rocks slightly exceeds the expected closure T for Ar-Ar (ca. 450 °C). Even though these veins contain very well preserved HP assemblages and mineral composition, the dates possibly represent the cooling ages rather than the crystallization ages. Nevertheless, these crack-seals contain typical HP assemblages, demonstrating that the reprecipitation of carbonates occurred at metamorphic conditions close the reconstructed decarbonation/dissolution processes. Other evidence for metamorphic reprecipitation of carbonate has been documented in Corsica. Intense metamorphic carbonation has been recently reported in the eclogitic units of Corsica in rocks of the metabasaltic suite (Piccoli et al., 2016), and may possibly testify for the migration of these carbonic fluids within the slab.

Experimental studies (Caciagli and Manning, 2003) and field observations (Ague and Nicolescu, 2014) indicate that carbonate dissolves in water congruently. In our case, this would imply that a fair amount of Ca is also released from pillow basalts during metamorphism and can interact with the surrounding lithologies. Part of this Ca was bound in silicates such as the newly-formed garnet.

## 10. Conclusion

Dehydration, decarbonation and carbonate dissolution accompany subduction of oceanic crustal sequences and release large amounts of C-O-H-bearing fluids. The exceptional lawsonite-eclogite facies rocks of Corsica provide insights into the interplay between these processes and their contributions to the C budget in subducting slabs. The studied

1030 samples indicate that structures and mineral assemblages inherited  
 1031 from seafloor hydrothermal alteration play an important role in the  
 1032 localization of important fluid–rock processes at HP conditions. Primary  
 1033 hydrothermal structures concentrating high amounts of carbonates may  
 1034 act as the preferential sites for fluid localization and fluid–rock interac-  
 1035 tions. Our data indicate that coupled hydration and decarbonation/  
 1036 dehydration processes driven by upward, up-T fluid flow are responsible  
 1037 for the release of significant amounts of carbonic fluids during prograde  
 1038 metamorphism. The calculated amount of CO<sub>2</sub> released by these  
 1039 reactions in the natural samples (20–70 kg per m<sup>3</sup> of reacted rock) is  
 1040 consistent with (or higher than) the estimates for decarbonation of  
 1041 metabasalts under open system behavior at comparable depths (17 kg  
 1042 per m<sup>3</sup>). Conversely, the calculated time-integrated CO<sub>2</sub> fluxes through  
 1043 the upper part of the subducted oceanic crust are potentially much  
 1044 greater than previously proposed cumulative fluxes that are generated  
 1045 throughout slab sections. The Corsican rocks indicate that only a portion  
 1046 of these fluids was released from the slab, whereas the rest was involved  
 1047 in successive intra-slab fluid–rock interactions leading to partial carbon-  
 1048 ate precipitation and decrease of dissolved carbon. Further effort will be  
 1049 necessary to integrate these data into a coherent model of fluid flow and  
 1050 fluxes through a complete section of subducting oceanic lithosphere.

1051 Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lithos.2018.01.028>.

## 1053 Acknowledgements

1054 **Q26** We thank DCO Reservoirs & Fluxes and ATM-MNHN for financial  
 1055 support of this project. Jeff Alt is thanked for inspiring discussions on  
 1056 the patterns of alteration of oceanic basalts. Stefano Poli and Jodie Miller  
 1057 are thanked for their reviews on this work, including very constructive  
 1058 and frank comments. Marco Scambelluri is thanked for editorial  
 1059 handling. Michel Fialin and Nicolas Rividi are thanked for technical  
 1060 assistance at Service Camparis. AVB thanks Paulette and Jean-Paul  
 1061 Santori for all the nice moments spent together since 2006. The authors  
 1062 acknowledge the facilities and the scientific and technical assistance  
 1063 of the Australian Microscopy & Microanalysis Research Facility at the  
 1064 Centre for Microscopy, Characterisation & Analysis, The University  
 1065 of Western Australia, a facility funded by the University, State and  
 1066 Commonwealth Governments.

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