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

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ABSTRACT

The interplay between the processes controlling the mobility of H₂O and C-bearing species during subduction 24 zone metamorphism exerts a critical control on plate tectonics and global volatile recycling. Here we present 25 the first study on fresh, carbonate-bearing, lawsonite eclogite-facies metabasalts from Alpine Corsica, France, 26 which reached the critical depths at which important devolatilization reactions occur in subducting slabs. The 27 studied samples indicate that the evolution of oceanic crustal sequences subducted under present-day thermal 28 regimes is dominated by localized fluid-rock interactions that are strongly controlled by the nature and extent 29 of inherited (sub)seafloor hydrothermal processes, and by the possibility of deep fluids to be channelized 30 along inherited or newly-formed discontinuities. Fluid channelization along inherited discontinuities controlled 31 local rehydration and dehydration/decarbonation reactions and the stability of carbonate and silicate minerals at 32 the blueschist-eclogite transition. Fluid-mediated decarbonation was driven by upward, up-temperature fluid 33 flow in the inverted geothermal gradient of a subducting oceanic slab, a process that has not been documented 34 in natural samples to date. We estimate that the observed fluid-rock reactions released 20–60 kg CO₂ per m³ 35 of rock (i.e. ~0.7–2.1 wt% CO₂), which is in line with the values predicted from decarbonation of metabasalts in 36 open systems at these depths. Conversely, the estimated time-integrated fluid fluxes (20-50 t/m²) indicate 37 that the amount of carbon transported by channelized fluid flow within the volcanic part of subducting oceanic 38 plates is potentially much higher than previous numerical estimates, testifying to the percolation of C-bearing 39 fluids resulting from devolatilization/dissolution processes operative in large reservoirs. 40

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53 1. Introduction

Altered oceanic crust is a major carrier of C in subduction zones 54 55 (dominantly as carbonate) (Staudigel, 2014), and its metamorphic evolution plays a critical role in controlling C fluxes to the deep mantle 56 or back to shallow reservoirs, as indicated by several experimental 57 58 (Hammouda, 2003; Poli et al., 2009; Keshav and Gudfinnsson, 2010; 59 Poli, 2015), numerical (Kerrick and Connolly, 2001; Gorman et al., 2006; Collins et al., 2015) and field-based studies (Li et al., 2012, 60 2014; Collins et al., 2015). 61

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https://doi.org/10.1016/j.lithos.2018.01.028 0024-4937/© 2018 Published by Elsevier B.V. The budget of carbonates at subduction zones depends on the 62 interplay between processes producing carbonic fluids, such as decar- 63 bonation reactions, carbonate dissolution and melting, and those 64 consuming carbon from the fluid in favor of carbonate precipitation, 65 such as carbonation and veining. The role of decarbonation reactions 66 (e.g. reactions between carbonates and silicates) on the carbonate 67 budget of subduction zones has been extensively investigated by exper- 68 imental and thermodynamic studies (Kerrick and Connolly, 2001; 69 Gorman et al., 2006; Poli et al., 2009; Gonzalez et al., 2016). Carbonate 70 dissolution (solubility of carbonate in a fluid at given pressure -P- and 71 temperature -T-) has been only recently introduced to the common ter- 72 minology of subduction-related processes (Frezzotti et al., 2011; Ague 73 and Nicolescu, 2014; Facq et al., 2014; Kelemen and Manning, 2015; Q13 Ferrando et al., 2017), and has been shown to play a major role in the 75

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production of carbonic fluids at forearc and subarc depths. Carbonate 76 77 melting is also an important process controlling the stability of carbonates (Poli, 2015); it takes place at P-T conditions much higher than those 78 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 infiltration of aqueous fluids in carbonate-bearing rocks (Gorman 86 et al., 2006; Frezzotti et al., 2011; Ague and Nicolescu, 2014). The tran-87 sition from blueschist- to eclogite-facies metamorphic conditions 88 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 omphacite and garnet) releasing considerable amounts of aqueous 92 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 carbonates as either solid or fluid phases (Gorman et al., 2006; Ague 96 97 and Nicolescu, 2014; Gonzalez et al., 2016; Piccoli et al., 2016).

98 Natural HP rocks exhumed in mountain belts provide an important means to study how the interplay between different CO₂-producing 99 and -consuming processes affects the carbonate budgets during subduc-100 tion of oceanic crust at the critical depth of 70-80 km where large 101 amounts of aqueous fluids are released. Moreover, natural samples 102 103 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 fluid flushing on carbonate dissolution in slab-forming rocks are 107 108 increasingly documented (Frezzotti et al., 2011; Ague and Nicolescu, 2014; Ferrando et al., 2017). Theoretical studies predict that also 109 decarbonation reaction and significant CO2 release may be induced by 110 upward fluid infiltration at depths corresponding to the blueschist-111 112 eclogite transition (Gorman et al., 2006). However, most field-based petrological studies of HP/LT carbonate-bearing lithologies have focused 113 on closed systems pointing to little decarbonation at these depths 114 (Cook-Kollars et al., 2014; Collins et al., 2015). Field evidence for 115 decarbonation of subducted rocks by upward, up-T fluid flow during 116 117 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 contributions to the fate of carbonates in subducted altered oceanic crust. 121 122 Here we provide the first study of these processes on fresh lawsonite eclogite-facies carbonated metabasalts by integrating field, textural, 123 geochemical and thermodynamic data from Alpine Corsica, together 124 with observations from weakly metamorphosed equivalents. Corsica 125 hosts exceptionally fresh lawsonite-bearing assemblages that are typi-126 127 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 by up-T fluid flow in a down-going oceanic slab at the critical zone 131 132 (70-80 km depth) where important petrological processes are predicted for most past (since the Phanerozoic; Tsujimori and Ernst, 133 2014) and active subduction settings (Syracuse et al., 2010) (Fig. 1). 134

135 2. Geological setting

Corsica, France, is a part of the Alpine orogenic system now isolated
from the European mainland by the opening of two Tertiary basins,
namely the Ligurian-Provençal and the Tyrrhenian basins (Jolivet
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 CaCO₃, Kelemen and Manning, 2015), and the breakdown boundaries of lawsonite in the Ca-Al-Si-O-H and MORB + H₂O 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 140 Alpine Corsica. Hercynian Corsica represents the largest part of the 141 island and was only weakly affected by the Alpine orogeny, with the 142 exception of the most external units of the Corsican paleo-margin 143 (External Continental Units, Fig. 2A) that underwent blueschist-facies 144 metamorphism during Alpine subduction. Alpine Corsica occupies 145 the northeastern part of the island and mainly consists of Tethyan 146 metaophiolites and metasediments of the Schistes Lustrés complex, 147 equivalent to the Ligurian-Piemonte units of the Western Alps (Caron 148 and Delcey, 1979; Lagabrielle and Lemoine, 1997; Vitale Brovarone 149 et al., 2013). Weakly metamorphosed equivalents of these units are 150 also exposed in the Nappes Supérieures (Rossi et al., 2002; Marroni 151 and Pandolfi, 2003), and represent a good proxy for Tethyan ophiolites 152 prior to Alpine metamorphism. The Schistes Lustrés complex comprises 153 several units that preserve their primary Tethyan tectonostratigraphic 154 coherence (mantle ultramafics \pm metagabbros followed upsection by 155 metavolcanics and metasedimentary cover rocks) but differ in their 156 structural, lithological and metamorphic features (Lagabrielle and 157 Lemoine, 1997; Vitale Brovarone et al., 2011a; Meresse et al., 2012; 158 Vitale Brovarone et al., 2013, 2014) (Fig. 2). This study focuses on the 159 Lawsonite-eclogite-facies unit. This unit consists of a well-preserved 160 section of a Tethyan ocean-continent transition lithosphere (OCT 161 in Fig. 2) characterized by lithological suites similar to slow-spreading 162 oceanic crust, such as serpentinites, metabasalts, and metagabbros 163 (Jurassic), together with the characteristic presence of slivers of 164 continental basement rocks interpreted as continental extensional 165 allochthons (Vitale Brovarone et al., 2011a; Meresse et al., 2012; 166 Beltrando et al., 2014). These rocks are capped by their primary 167 Mesozoic metasedimentary cover rocks. 168

2.1. Metamorphic evolution of lawsonite eclogites in Alpine Corsica 169

The Alpine metamorphism in the Schistes Lustrés ranges from low- 170 grade blueschist-facies (ca. 350 °C, 1.5 GPa) to lawsonite eclogite- 171 facies conditions (ca. 530 °C, 2.3 GPa) (Fig. 1). A recent review of the 172 available P-T estimates including a belt-scale thermometric dataset 173 can be found in Vitale Brovarone et al. (2013) (see also Vitale 174 Brovarone et al., 2014 for updates), and only the main metamorphic 175 features of the lawsonite eclogite-facies terranes are reported in the 176 following. Lawsonite eclogite-facies rocks in Alpine Corsica are well 177

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

201Overall, the reconstructed prograde P-T evolution matches the range202of 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

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 representative 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

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

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

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

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

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

Metabasalts are widespread in the lawsonite-eclogite-facies unit
and form large bodies locally extending for several tens of km. The samples selected for this study are from two localities: the Défilé de Lancône
and Monte San Petrone areas (Fig. 2, and S1 for structural relationships)
(Miller et al., 2000; Ravna et al., 2010; Vitale Brovarone et al., 2011a,
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 Défile 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.

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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.

302 4.1.1. Group 1: metamorphosed seafloor hydrothermal veins

Different types of seafloor hydrothermal veins are distinguished 303 (Figs. 4A, B, 6A-E). Some pillow metabasalts preserve the 'heater-like' 304 structures characteristic of hollow pillows. These structures typi-305 cally consist of cm-thick carbonate-rich parallel veins preserved in 306 the pillow's core and extending outward to a more complex net-307 work of thinner, randomly oriented veins (Fig. 6B,C; see also 308 309 Fig. 3A for low-grade precursor). In other cases, carbonate is only 310 found as randomly-oriented veins filling igneous cooling fractures in undeformed metabasalt (Figs. 4B, 5B, 6E). The carbonate in these 311 structures may have two possible origins: hydrothermal carbonate pre- 312 cipitating from seawater circulation, or sedimentary carbonate filling 313 open fractures. A hydrothermal origin is preferred for most of our sam- 314 ples based on the collected dataset (see sample description). Owing to 315 surface carbonate dissolution, these rocks are rarely preserved on the 316 weathered surface (Fig. 6E). Despite that, fresh samples were found 317 both along the Défilé de Lancône in the interior of large pillow basalts, 318 and at San Petrone. 319

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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 metaberceias (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. The cartoon shows two types of 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.)

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320 4.1.2. Group 2: carbonated metabasalts sensu stricto

321 Carbonated metabasalts sensu stricto are herein distinguished from the other carbonate-bearing metabasalts. In these rocks, the carbonate 322 323 is diffusely distributed in the matrix of undeformed metabasalts and is most probably the result of seafloor hydrothermal replacement of 324 primary olivine or filling of disseminated vesicles (Alt and Teagle, 325 1999), rather than crack-filling precipitation processes. These rocks 326 are most typically found as metabasaltic clasts or matrix material in 327 328 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 the metabasaltic suite of the San Petrone area, whereas they are rarer 333 334 in the Défilé de Lancône suite. Most of them were stretched and made subparallel to the main regional foliation, but some still show clear 335 336 crosscutting relationships with the deformed metabasalt hosts (Healy et al., 2009; Ravna et al., 2010; Vitale Brovarone et al., 2011b). The 337 typical assemblage consists of rod-shaped carbonate and omphacite, 338 together with coarse-grained phengite; apatite and rare garnet can be 339 340 easily identified in hand specimen.

341 4.1.4. Group 4: deformed carbonate-bearing metabasalts

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

349 5. Sample description and mineral chemistry

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

359 5.1. Group 1: Metamorphosed seafloor hydrothermal veins

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

363 5.1.1. Large carbonate veins in pillow metabasalts

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

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

Calcite is the dominant *Ca carbonate* polymorph in the rock. Nevertheless, Raman spectroscopy revealed the preservation of aragonite
included in garnet, lawsonite, and pyrite (Fig. S2), as also observed in
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, guartz, 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 zona- 386 tion 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 idioblastic 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.

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 idioblastic 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).

Epidote is found in two main microstructural positions, (1) as 429 inclusions in garnet (Ep1) $[Fe^{3+} / (Fe^{3+} + Al) = 0.16]$ (Fig. 8B); 430 (2) as texturally late pseudomorphic products after garnet (Ep2a) 431 $[Fe^3 / (Fe^3 + Al) = 0.18]$, matrix lawsonite (Ep2b) $[Fe^3 / (Fe^3 + Al) = 432 0.07]$ (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 μ 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

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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 Za1ternating 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.)

relative modal amounts of the different garnet types vary from one to 443 another thin section. Garnet showing intermediate features between 444 445 Gt1 and Gt2 are also observed. Both garnet types locally include sulfides. Zoned crystals of amphibole with glaucophane cores and actinolite rims 446 are widespread. Isolated actinolite crystals are also found, and may be 447 either a peak or a retrograde phase. *Chlorite* aggregates are deep green 448 and pseudomorphically replace garnet and amphibole. Chlorite has 449 450 Mg# of 0.56–0.58 (Mg/[Mg + Fe²⁺]). Pyrite forms sub-idiomorphic crystals or aggregates, and includes lawsonite, carbonate, and quartz. 451 Quartz is common as inclusions in lawsonite, garnet, and pyrite 452 (Fig. 8C,E,F–G). In the matrix, quartz is scarce in the presence of Gt1, 453 but is more abundant in the vicinity of Gt2 (Fig. 8I). Albite is widespread 454 455 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). However, the albite inclusions are systematically connected by late 458 cracks and are interpreted as a retrograde replacement of former inclu-459 sions. Tiny apatite crystals are disseminated in the rock's matrix. 460

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

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

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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 idiomorphic 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, and lawsonite carbonate 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

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

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

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

512 We performed whole-rock carbonate δ^{13} C and δ^{18} O analyses on four 513 samples from the Défilé de Lancône and San Petrone areas (Table 1), 514 as well as in-situ δ^{18} O garnet isotope analysis by SIMS in order to investigate the possible contribution of decarbonation reactions to the 515 isotopic signature of newly-formed Ca-rich garnet. 516

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

For in-situ δ^{18} O garnet analyses, we selected garnet crystals with 528 alternating Ca-poorer and Ca-richer zones (patchy, Mn-poor Gt2, 529 Fig. 12B) in sample Lancône-pillow. Sixty point-analyses were per- 530 formed in cut thin sections on six garnet crystals, and yield average 531 δ^{18} O values of $5.1 \pm 0.4\%$ (2SDDDDn = 41DD) and $4.83 \pm 0.4\%$ Q16Q17 (2SDDDDn = 19DD) for the Ca-poorer and Ca-richer garnets, respec- 533 tively (Fig. 12C). Using bulk Ca carbonate and in-situ garnet δ^{18} O values 534 for sample Lancône-pillow, and the oxygen fractionation factors by 535 Zheng (1993), a T of ~500 °C was obtained for the carbonate-garnet q18 equilibrium, which is consistent with other temperature estimates in 537 this area.

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7. Garnet formation and decarbonation reactions

539

Omp+Law+Gt Cc (+Araq) B ٢c (+Arag) Dmr Cc (+Arag) Omp 200um

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) pseudohexagonal 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 reequilibration in the inherited vein. Note the presence of garnet, zoned omphacite and lawsonite, the latter being concentrated at the vein wall (bottom-right).

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 546 xenomorphic inclusions of lawsonite, aragonite, quartz \pm Ep (Fig. 8E–G). 547 The relict reactants included in the garnets thus suggest the reactions: 548

$$\label{eq:Lawsonite} \begin{array}{l} \text{Lawsonite} + 2 \mbox{ Aragonite} + \mbox{Quartz} = \mbox{Grossular} + 2 \mbox{ CO}_2 + 2 \mbox{ H}_2 \mbox{O} & \mbox{(1)} \\ & \mbox{550} \\ & \mbox{551} \end{array}$$

2 Clinozoisite + 5 Aragonite + 3 Quartz = 3 Grossular + 5 $CO_2 + H_2O$

(2)

553

The common presence of quartz as inclusions in garnet and the textural dependence of Gt1 and Gt2 development on the availability of 554 local quartz are consistent with these prograde reactions. The relative 555 contributions of reactions (1) and (2) in the sample are variable, and 556 depend on the extent of local re-equilibration of the sample (i.e. Ep1 557 to lawsonite) prior to garnet formation. Gt2 is texturally associated 558 with Ep1 (Fig. 81), and the chemical homogeneity of Gt2 and Ep1 559 suggests that the two phases have reached equilibrium by exchanging 560 compositions via Reaction (2) and the redox reaction: 561

$$3 \text{ Epidote} = \text{Almandine} + 2 \text{ Grossular} + 1.5 \text{ H}_2\text{O} + 0.75 \text{ O}_2$$
(3)

In this reaction, O₂ is included only as a redox indicator, but not considered as a fluid species in mass balance analysis due to its infinitesimal 564 concentration. 565

The presence of Mn- and Fe-rich garnet zones indicates that at least 566 one additional mafic mineral, likely prograde chlorite, participated in 567 the garnet-forming reactions. Reactions (2) and (3) can be coupled to 568 account for the measured composition of Ep1 included in Gt2: 569

$$\begin{split} & [0.48 \ Epidote + 0.52 \ Clinozoisite] + 1.3 \ Aragonite + 0.78 \ Quartz \\ &= 0.16 \ Almandine + 1.1 \ Grossular + 0.5 \ H_2O + 1.3 \ CO_2 + 0.12 \ O_2 \\ & (4) \end{split}$$

571

The garnet composition resulting from reaction (4) between epidote and carbonate is enriched in grossular component $[X_{Crs} = 0.87; X_{Alm} = 572]$ 0.13], in contrast to the composition of Gt2 in the sample [$X_{Grs} = 0.4$; 573 $X_{Alm} = 0.6$]. Taking the composition of Gt2 as a proxy, the garnet forma-574 tion resulted from decomposition of the former minerals clinozoisite/ 575 epidote, aragonite, quartz, and additional Fe-Mg-Mn-bearing minerals 576 (e.g., seafloor hydrothermal celadonite and/or Fe-oxyhydroxides; pro- 577 grade chlorite, amphibole). It is worth noting that the reaction between 578 hydrous silicate and carbonate ((1) and (2)) consumes a significant 579 amount of quartz in the rock. These reactions could not take place in 580 standard silica-undersaturated metabasalts, whereas they are favored 581 in seafloor hydrothermal products containing free quartz as a reactant, 582 as observed in the seafloor hydrothermal products preserved in the 583 Corsica metabasalts (Figs. 3, 4C). Nevertheless, our data suggest that 584 the size and initial mineral assemblage of the inherited hydrothermal 585 veins controlled the extent of fluid channelization and magnitude of 586 decarbonation reactions in the rock. As an example, Ep1-bearing large 587 inherited veins in hollow pillow metabasalts (see Figs. 4C,D, 5A, 6B) 588 show extensive decarbonation reactions, whereas Ep-1-free small, 589 inherited cooling fractures in metapillow cores (see Figs. 4A,B, 5B, 6E) 590 do not. 591

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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 \pm 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

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

We used the internally-consistent thermodynamic dataset of Holland and Powell (1998), a MATLAB-based code package to perform the thermodynamic calculations (Chu and Ague, 2013), and updated activity models (garnet: White et al., 2007; epidote: Holland and 604 Powell, 1998; H₂O-CO₂: 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_{Alm} = 60; X_{Grs} = 40; 607 Ep1: XEp = 16; X_{Zo} = 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_{CO_2}) (reactions (1) and (2)) or oxygen fugacities (f_{O_2}) (reaction (3)) 614 (Fig. 14). For reactions (1) and (2), the assemblage at higher T reaches 615 equilibrium with a higher- X_{CO_2} fluid. The assemblage epidote + garnet 616



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

12

Table 1

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t1.2 Selected samples and analytical strategy.

1.3	Sample	Group	Locality	Facies ^a	Peak T ^a	Peak P ^a	Petrography	Mineral chemistry	Thermodynamic modeling	Carbonate bulk $\delta^{13}C-\delta^{18}O$	$\begin{array}{c} \text{Garnet} \\ \text{in-situ} \\ \delta^{18}\text{O} \end{array}$	Phengite Ar-Ar
1.4	2cor14-2	1	San Colombano	Sub-greenschist	300 °C	0.4 GPa	Х	Х				
1.5	Cor16-62a	1	Bocca di Serna	Sub-greenschist	300 °C	0.4 GPa	Х	Х				
1.6	Cor16-62b	2	Bocca di Serna	Sub-greenschist	300 °C	0.4 GPa	Х	Х				
t1.7	Lancône-pillow	1	Défilé de Lancône	Lawsonite-eclogite	450-500 °C	1.9-2.6 GPa	Х	Х		Х	Х	
1.8	OF3156	1	San Petrone	Lawsonite-eclogite	500–540 °C	2.2-2.4 GPa	Х	Х				
1.9	Lancône12-6	1	San Petrone	Lawsonite-eclogite	500–540 °C	2.2-2.4 GPa	Х	Х	Х	Х		
1.10	OF3322	3	San Petrone	Lawsonite-eclogite	500–540 °C	2.2-2.4 GPa	Х	Х		Х		Х
1.11	2COR12-8/M9-53a ^b	3	San Petrone	Lawsonite-eclogite	500–540 °C	2.2-2.4 GPa	Х	Х		Х		Х
t1.12	2COR12-11/M953bb	3	San Petrone	Lawsonite-eclogite	500–540 °C	2.2-2.4 GPa	Х	Х		Х		Х
1.13	Acor14-16a,c	4	Défilé de Lancône	Lawsonite-eclogite	450-500 °C	1.9–2.6 GPa	Х	Х				

t1.14 ^a See text for references.

t1.15 ^b 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 assemblage is in equilibrium with a fluid of higher X_{CO_2} (dashed curves 619 620 in Fig. 14) than the lawsonite-bearing assemblage (solid curves in 621 Fig. 14). The f_{0_2} contours of reaction (3) are sensitive to pressure, as 622 discussed by Donohue and Essene (2000) for equivalent redox reactions. The epidote and garnet of interest, if equilibrated at higher P, 623 suggest more oxidized conditions than in a low-P assemblage. 624

In this calculation, we assume that the mineral assemblage recorded 625 the equilibrium with the fluid at one specific P-T condition along the 626 627 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 2.2 GPa Ravna et al., 2010; Vitale Brovarone et al., 2011b). We thus 631 632 reasonably assume that garnet formation in local (meta-) stable domains occurred at or close to peak P-T metamorphic conditions, 633 where the fluid X_{CO_2} is about 0.2–0.4 mol%, with the f_{O_2} ~FMQ + 1. The 634 estimated X_{CO_2} at the peak conditions is reasonably consistent with 635 019 the CaCO₃ solubility in water (~0.2 mol%, Caciagli and Manning, 2003).

When the fluid flows along a T and/or P gradient, the fluid changes 637 its composition in response to the changes in P-T conditions, which re-638 flects the reaction progress. For the devolatilization reaction (1), when 639 1 mol grossular is precipitated in the rock, 2 mol CO₂ and 2 mol H₂O 640 641 are released to the fluid. For reaction (2), 1 mol grossular corresponds 642 to 5/3 mol CO₂ and 1/3 mol H₂O. Accordingly, if the devolatilization pro-643 cesses were taking place in a closed system, CO₂ would be greatly 644 enriched in the fluid with small reaction progress (Greenwood, 1975). However, if the fluid is in equilibrium with the garnet-forming matrix 645 646 along the flow path, the time-integrated flux can be thus estimated based on fluid mass conservation (Baumgartner and Ferry, 1991; See 647 Supplementary Material for details and discussions). Calculations are 648 conducted to estimate the time-integrated fluid flux into the rock to 649 drive the devolatilization reactions at any P-T condition along the pro-650 651 grade P-T path, assuming that fluid flow was predominantly vertically 652 upward through the metabasalt unit.

The time-integrated fluid flux (m^3/m^2) and CO_2 flux (g/m^2) cor-653 responding to garnet precipitation (1 g garnet per 1 m³ rock) are 654 presented in Fig. 15. At P-T conditions close to the prograde path, 655 1 g garnet ($X_{Grs} = 0.4$) precipitates in 1 m³ rock in response to 656 0.01–0.02 m³ H₂O-CO₂ fluid flowing through 1 m² into the rock. 657 The infiltrating fluid flux contains $50-70 \text{ g/m}^2 \text{ CO}_2$, depending on 658 the specific reactants and P-T conditions. We do not imply that the 659 mineral assemblages were in equilibrium with the fluid throughout 660 the prograde metamorphism, but the flux expression above depends 661 on the fluid compositional gradient rather than the absolute values. 662 The simulations by Ague (1998) demonstrate that even in disequilib-663 rium, compositional gradients approach the local equilibrium case 664 665 along the majority of the flow path, so the flux estimates based on equilibrium assumption are still valid. We also note that the different 666 P-T conditions do not cause order-of-magnitude differences in the 667 fluid flux estimates. 668

If the preserved mineral compositions reflect the peak stage then, 669 for instance, 1 g garnet product in 1 m³ rock by local devolatilization 670 reactions corresponds to about 0.01 m³/m² fluid flux flowing through 671 (including ~70 g/m² CO₂). The fluid flux is a cumulative effect of 672 devolatilization of the whole subduction section, so it is much larger 673 than that generated from local devolatilization reactions where garnets 674 are formed. 675

The garnet amount in our samples reaches ~20 vol%. We estimate 676 that the garnet amount produced by the reactions between carbonates, 677 epidote/lawsonite and guartz accounts for at least 40% of total garnet 678 (8 vol% taking 20 vol% garnet in the rock; taking Gt2 and reaction (2) 679 as a proxy for garnet). Moreover, the remaining 12 vol% is much 680 larger than the garnet mode in the carbonate-free metabasalts, so it 681 is highly likely that several other carbonate-consuming reactions 682 took place in the rock. Taking 8 and 20 vol% garnet to correspond 683 to 3×10^5 and 7.6×10^5 g per 1 m³ rock, respectively, yields upper 684 and lower limits of the estimate of the fluid flux through the rock 685 of 3×10^3 and 7.6×10^3 m³/m². These values are in agreement 686 with estimated time integrated fluid fluxes in crustal metamorphic 687 settings, and plot transitionally between flux ranges typically recog- 688 nized in dominantly pervasive $(<10^{3} \text{ m}^{3}/\text{m}^{2})$ and highly channel- 689 ized $(>10^{4} \text{ m}^{3}/\text{m}^{2})$ flow systems (Ague, 2014) The values are, 690 however, much higher than the time-integrated fluid flux proposed 691 at the top of an oceanic slab for a vertical flow $(3 \times 10^2 \text{ m}^3/\text{m}^2; 692)$ Zack and John, 2007). The time-integrated fluid flux leading to the 693 garnet precipitation carried a CO_2 flux as high as $20-50 \text{ t/m}^2$. 694

9. Discussion

695

9.1. Origin and significance of the carbonated metabasalts of Alpine Corsica 696

Considerable effort has been made to estimate the amount of car- 697 bonate incorporated in oceanic basalts and its role as a carrier of C 698 into active subduction (Staudigel et al., 1996; Jarrard, 2003; Staudigel, 699 2003). The study of metamorphic rocks formed tens of Ma ago (i.e. in 700 the Jurassic for the Corsica samples) also requires consideration of 701 long-term variation over geological timescales (Jarrard, 2003). Gillis 702 and Coogan (2011) reviewed data from seven DSDP/ODP drill cores, 703 and concluded that the carbonate content of the upper 300 m of the vol-704 canic crust is higher in the slower-spreading Atlantic (0.8–4.2 wt%) than 705 in the Pacific (0.2–2.6 wt%) crust. In both settings, the Mesozoic crusts 706 are 2 to 13 times richer in carbonate than the Cenozoic ones (Gillis 707 and Coogan, 2011). The Corsican basalts originated in a Mesozoic, 708 Tethyan ocean-continent transition zone characterized by an overall 709 crustal architecture typical of slow-spreading oceans (Lagabrielle 710 and Lemoine, 1997; Lagabrielle et al., 2015). Therefore, in terms of C 711

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Fig. 12. (A) Diagram summarizing the whole rock carbonate ($\delta^{18}O$ and $\delta^{13}C$) and in-situ garnet ($\delta^{18}O$) stable isotope data. Previous data on eclogite-facies metabasites from Corsica are also reported (after Miller et al., 2001). The calculated $\delta^{18}O$ 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 H₂O 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 $\delta^{18}O$ values by SIMS.

content, the Corsica metabasalts can be considered as a carbonate-rich 712 end-member. 713

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 com-716 monly 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 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_{CO2} fluid composition (Nitsch, 1972), Q20 (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_{CO2} 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 Beyssac, 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

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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.

complex role of fluid infiltration in the coupling between hydrationand dehydration/decarbonation processes during the metamorphic

778 evolution of subducting slabs.

779 9.3. Carbon and oxygen isotopic fingerprints of metamorphic decarbonation

Variations in δ^{13} C and δ^{18} O values for carbonate in metamorphic rocks are used as markers for decarbonation processes in subduction zones. For example, Cook-Kollars et al. (2014) and Miller et al. (2000, 2001) provided large datasets on C and O isotopic data on carbonatebearing rocks from the Western Alps and Alpine Corsica. Both studies noticed little shift in δ^{13} C relative to the inferred marine signature (0%), 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 mélange (Greece) show very 788 little decrease in δ^{13} C relative to unaltered rocks (Ague and Nicolescu, 789 2014), indicating that the interpretation of δ^{13} 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 δ^{13} 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

2.1 Table 2.

2.1	I dDie 2.																
2.2		Lancône-pillow		Lancône12-6		Lancône12-6			Lancône12-6			Lancône12-6		OF3322	2		
2.3 2.4		Gt2 Dark	Gt2 Bright	Gt1	Gt2		Ep1	Ep2 after Gt	Ep2 after Law		Blue-Amp	Green-Amp		Chl		Phe	Phe
2.5	SiO ₂	37.67	36.67	37.63	38.28	SiO ₂	38.52	38.66	40.38	SiO ₂	57.53	57.12	SiO ₂	26.83	SiO ₂	53.47	53.64
2.6	Al_2O_3	18.57	20.64	21.03	20.76	Al_2O_3	27.78	26.94	30.89	Al_2O_3	10.54	7.96	Al_2O_3	19.83	Al_2O_3	23.43	23.12
2.7	TiO ₂	0.01	0.11	0.12	0.18	MgO	0.02	0.00	0.02	TiO ₂	0.00	0.10	MgO	23.34	TiO ₂	0.07	0.13
2.8	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
2.9	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
2.10	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
2.11	CaO	23.95	11.69	11.38	14.08	Na ₂ O	0.09	0.02	0.21	CaO	0.92	4.49	Na ₂ O	0.10	CaO	0.06	0.05
2.12	Na ₂ O	0.00	0.00	0.04	0.03	K ₂ O	0.03	0.00	0.01	Na ₂ O	6.93	5.18	K ₂ O	0.03	Na ₂ O	0.12	0.09
2.13	K20	0.00	0.01	0.00	0.01	Cr_2O_3	0.00	0.00	0.00	K20	0.00	0.04	Cr_2O_3	0.00	K ₂ O	10.63	10.78
2.14	Cr_2O_3	0.00	0.04	0.00	0.02	Total	97.51	97.39	98.35	Cr_2O_3	0.07	0.00	Total	87.24	Total	95.43	95.59
2.15	Total	98.75	99.81	100.47	100.58					Total	97.66	98.25					
2.16						Si	2.99	3.01	3.06				Si	5.61	Si	3.57	3.58
2.17	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
2.18	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
2.19	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 ³⁺	0.00	0.00
2.20	Ti	0.00	0.01	0.01	0.01	Fe ⁺³	0.48	0.53	0.21	Ti	0.00	0.01	Fe ³⁺	0.04	Fe ²⁺	0.17	0.17
2.21	Cr	0.00	0.00	0.00	0.00	Mn	0.01	0.00	0.02	Cr	0.01	0.00	Fe ²⁺	4.04	Mn	0.00	0.00
2.22	Fe ³⁺	0.21	0.05	0.02	0.02	Mg	0.00	0.00	0.00	Fe ³⁺	0.21	0.05	Mn	0.05	Mg	0.46	0.47
2.23	Fe ²⁺	1.02	1.98	1.93	1.72	Ca	1.96	1.97	1.89	Fe ²⁺	1.27	1.33	Mg	5.23	Ca	0.00	0.00
2.24	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
2.25	Mg	0.00	0.01	0.06	0.05	K	0.00	0.00	0.00	Mg	1.82	2.34	Na	0.08	К	0.90	0.92
2.26	Ca	2.04	1.01	0.97	1.19	Total	7.99	7.99	7.97	Ca	0.14	0.67	K	0.02			
2.27	Total	9.27	8.03	8.00	7.99	ХЕр	0.2	0.2	0.1	Na	1.86	1.40	Oxygens	28			
2.28	XCa	0.62	0.33	0.32	0.40					K	0.00	0.01	XMg	0.56			
2.29	XMg	0.00	0.00	0.02	0.02					Oxygens	23	23					
2.30	XFe	0.38	0.66	0.65	0.58												
Q5	XMn	0.00	0.01	0.01	0.01												

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Fig. 14. Diagram illustrating the stable or metastable equilibria among lawsonite, epidote and garnet at specific X_{co2} (mol%) and f_{o2} (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;
 Q4 Ep: epidote; Gt: garnet; Fld: fluid. See text for details.

798 $(>20 \text{ t/m}^2 \text{ of } \text{CO}_2)$, suggesting that the isotopic composition of C in this fluid may have contributed to the final δ^{13} C composition of residual car-799 bonate. If the incoming fluid was derived from dissolution of marine 800 carbonate following the patterns observed by Ague and Nicolescu 801 (2014), the final δ^{13} C values of the residual carbonate would not have Q2 changed significantly in the studied rocks. The δ^{13} C values of carbonate 803 804 in the metamorphic crack-seals are consistent with transport of carbon preserving marine isotopic signatures. In sum, we conclude that the 805 absence of significant shifts in δ^{13} C values does not necessarily imply 806 that little decarbonation occurred. 807

808 The δ^{18} O values (9–11‰) of carbonate in the selected set of samples 809 are lower than the average composition of carbonate in the Corsican 810 metaophiolite 12-20‰, Miller et al., 2001) (Fig. 12C). Miller et al. 811 (2001) interpreted the average values in the HP metabasaltic rocks of 812 Corsica as evidence for the absence of large-scale, pervasive fluid flow and isotopic homogenization of the subducted altered oceanic crust. 813 814 Conversely, our samples testify for isotopic equilibration at near peak conditions (see Section 6). This feature further suggests that the 815 selected set of samples recorded channelized fluid flow enhancing 816 isotopic equilibration of marine carbonates with silicates in the 817 818 metabasaltic rocks at HP conditions. The collected in-situ δ^{18} O garnet 819 data may constrain the timing and conditions for this equilibration. 820 Ca-silicates resulting from decarbonation reactions in our samples are expected to inherit at least part of the δ^{18} O of the precursor carbonate, 821 unless the rock δ^{18} O is buffered by the signature of the incoming fluid. 822 However, if the reactant carbonate and/or the incoming fluid are equil-823 ibrated with the metabasic host rocks, the decarbonation reaction may 824 not be obviously deduced by the δ^{18} O signature. The δ^{18} O values of 825

3.1	Table 3	

t3.2		d13C PDB	d180 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 826 any significant shift relative to the Ca-poorer garnet (Fig. 13B). The 827 absence of significant δ^{18} O variations between the garnet generations 828 suggests that the system was buffered by an external fluid source rather 829 than by local "closed" equilibria. The latter hypothesis would suggest 830 that the infiltrating fluid had a δ^{18} O signature equilibrated with the 831 metabasaltic sequence (6–11‰) in the Défilé de Lancône, (Miller Q22 et al., 2001). The δ^{18} O composition of carbonate in the metamorphic 833 veins (about 11‰) supports this hypothesis. 834

9.4. Role of inherited seafloor hydrothermal structures on devolatilization 835 and C circulation in subduction zones 836

The modes of carbonation and the spatial distribution of carbonate 837 in the rock require additional discussion. Carbonate incorporation in 838 the oceanic crust can be strongly inhomogeneous and localized (see 839 Section 9.1). Owing to the complexity and variability of alteration pat- 840 terns, global budgets do not account for the spatial distribution of the 841 carbonates at the meso and microscale. Most thermodynamic studies 842 investigating the general decarbonation patterns of oceanic subduction 843 consider averaged oceanic basalt compositions (e.g. "Supercomposite" 844 bulk composition of Staudigel et al., 1989) that cannot reproduce this 845 variability. The choice of using an average composition is valid in the 846 case of decarbonation reactions that do not directly correlate to the 847 amount of carbonate in the rock, but may result in significant underes- 848 timations of the total produced C fluxes if carbonate dissolution is also 849 relevant. As an example, decarbonation can be limited in carbonate- 850 rich systems poor in silicates (Kerrick and Connolly, 2001; Gorman 851 et al., 2006; Cook-Kollars et al., 2014). Carbonate-rich, silicate-poor 852 hydrothermal veins may undergo little decarbonation compared to 853 mixed carbonate-silicate assemblages, as also suggested by our data; 854 conversely, fluid channelization along veins may potentially cause 855 total carbonate dissolution (Ague and Nicolescu, 2014). Therefore, 856 inherited hydrothermal systems may exert a chemical/structural feed- 857 back on C release in subduction zones. 858

The collected data show that large-scale chemical homogenization 859 of subducted oceanic metabasalts is not necessarily achieved at forearc 860 depths (see also conclusions by Miller et al., 2001), thus preserving 861 localized domains containing carbonate amounts several times higher 862 than the averaged compositions of altered oceanic basalts. This preser- 863 vation is not only characteristic of the lawsonite-eclogites of Corsica, 864 but is also observed in the blueschist- and eclogite-facies rocks from 865 the Western Alps and other orogenic belts (Collins et al., 2015). There- 866 fore, our samples can provide important insights on the potential role 867 of structural inheritance on the patterns of C loss from subducted 868 metabasalts.

Inherited hydrothermal vein networks are structures that may favor 870 fluid channelization and fluid-rock interactions during subduction, 871 as summarized in Fig. 16. The studied samples from Corsica provide 872 the first natural evidence for such an effect, as demonstrated by the 873 documented fluid-mediated isotopic reset, the coupled hydration-874 decarbonation reactions, and the estimated time-integrated fluid fluxes testifying for channelized fluid flow (see Section 8). 876

The composition (mineralogical and chemical) of the inherited 877 hydrothermal material also plays an important role on the patterns of 878 C release during subduction. The particular Ca-Al-Si-C-rich (and Fe-Mg 879 poor) compositions (high initial carbonate, epidote, quartz) of the 880 inherited hydrothermal veins may also be an important factor favoring 881 decarbonation reactions that have been shown to be hampered in stan-882 dard metabasaltic compositions where carbonate phases other than 883 Ca carbonate are present (Kerrick and Connolly, 2001; Poli et al., 884 2009). The Fe-Mg-poor assemblages of the Corsica rocks play a key role in the development of the proposed decarbonation reactions. 886 These particular bulk-rock compositions (together with other parame-887 ters such as f_{O2}) are probably responsible for the absence of Mg-Fe 888 carbonates in our high-pressure assemblages, and may also have a 889

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Fig. 15. Calculated time-integrated fluid flux (m³/m², A, C) and CO₂ flux (g/m², 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.

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

Moreover, the chemical/mineralogical composition of these veins may exert a positive feedback on permeability, fluid channelization and decarbonation. Wark and Watson (2002) demonstrated experimentally that the mineral assemblage strongly controls grain-scale pore channelization in systems controlled by T or compositional gradients. They showed that calcite-quartz-wollastonite rock is much 897 more suitable for channelization than rock composed of calcite alone. 898 This channelization effect is also documented in natural HP fluid- 899 mediated systems (Molina et al., 2004). Nevertheless, in our rocks, 900 decarbonation is particularly efficient in inherited hydrothermal 901 veins containing initial carbonate, quartz and epidote, whereas it 902 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.

904 (Supplementary material). This may be due to the interplay between 905 mineralogical/permeability factors (Wark and Watson, 2002), even though this effect can be hampered by the progression of the decarbon-906 907 ation reactions (Balashov and Yardley, 1998). Last, fluid channelization along inherited hydrothermal systems can mobilize elements hosted 908 in typical oceanic hydrothermal deposits, such as S and metals. Al-909 though our study did not focus on these elements, the studied samples 910 contain possible evidence for transformation of sulfide deposits in the 911

912 subducted metabasaltic suite (Figs. 4D, 6C).

913 9.5. Implications for deep C fluxes at subduction zones

Our study reports the first example of decarbonation reactions 914 915 driven by fluid infiltration in a subducted segment of oceanic crust. The overall setting and field relations are consistent with the model of 916 simple vertical fluid flow. Considering a standard geothermal model 917 918 for the Corsica subduction (T increasing from the inner slab towards the overlying mantle wedge), this setting corresponds to decarbonation 919 driven by an upward, up-T fluid flow. The cumulative time-integrated 920 fluid flux passing through the rock and leading to the garnet precipita-921 tion carried a CO₂ flux as high as 20–50 t/m² (0.5–1.1 Mmol/m²). For 922 923 comparison, decarbonation induced by the interaction between this 924 fluid and the carbonate-bearing metabasalts would release 20-60 kg 925 CO_2 from 1 m³ rock considering reaction (1) or (2). The lower limit is close to the infiltration-driven decarbonation model of Gorman et al. 926 (2006) (~0.5 wt% CO₂, corresponding to 17 kg CO₂ from 1 m³ rock). 927

In the Corsican slab, the basaltic section was thinner than 500 m, 928 929 as indicated by lithostratigraphic observations in both low-grade 930 units and their higher-grade equivalents (Miller et al., 2001; Vitale 931 Brovarone et al., 2011a); a column of 500 m of such rock only releases 932 10–30 t/m² CO₂. The deficiency of CO₂ flux suggests that the majority 933 of CO₂ flux must be derived from deeper units of the subducting slab. 934 The studied sequence consists of basal serpentinites (\pm metagabbro 935 pods), metabasalts and metasedimentary cover rocks. Although the metasedimentary cover is locally thick (>200 m) in this sequence, pre-936 vious tectonostratigraphic reconstructions suggest that the polarity of 937 938 the studied unit was upright during subduction and was only later 939 affected by large-scale folding and overturning during exhumation (Vitale Brovarone et al., 2013). Therefore, it can be assumed that the 940 primary cover of this piece of subducted oceanic lithosphere did not 941 contribute to these fluxes, and that the extra fluxes infiltrating the 942 943 metabasaltic sequence were mainly contributed by the underlying serpentinites, in line with the measured garnet and carbonate isotopic 944 signature. Alternatively, or in addition, if the documented fluid-rock in-945 946 teractions occurred after the detachment of the eclogite units along the plate interface, any other underlying subducting rocks (metasediments, 947 948 metaigneous, serpentinites) may have contributed to these fluxes.

The peak pressure (2.2–2.3 GPa) roughly corresponds to the forearc 949 depth of the fluid flux pulse from the subducting slab (Gorman et al., 950 2006). We compare our results with those predicted by the model of 951 Gorman et al. (2006) at the same depths. For that, we calculated a hypo-952 953 thetical subduction rate for Corsica by using the available constraints on 954 the age of blueschist-facies (37 Ma; 1.8 GPa) and eclogite-facies (34 Ma; 955 2.3 GPa) metamorphism (Martin et al., 2011; Vitale Brovarone and 956 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 esti-957 958 mates 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-959 960 integrated CO₂ flux can be converted to 4–9 Mmol/yr per kilometer of arc length. These values are comparable to the cumulative predictions 961 from phase equilibria analysis for cool subduction zones by Gorman 962 963 et al. (2006) (≤3 Mmol/yr for the distillation decarbonation model and ≤13 Mmol/yr for the infiltration decarbonation model). However, we 964 note that the thickness of metabasalt in the Corsican slab (\leq 500 m) is 965 thinner than the model in Gorman et al. (2006) (2 km). Moreover, the 966 967 carbonate-bearing marine sediment contributes more than half of the cumulative carbon flux in Gorman et al.'s (2006) infiltration model, 968 but such a layer is commonly thin or absent on the top of Corsica 969 units. Thus, the general model of Gorman et al. (2006) cannot be 970 directly applied to the Corsican study. If the contributions from the 971 marine sediments and more than half of the metabasalt are removed 972 from Gorman et al.'s (2006) model, the predicted cumulative time- 973 integrated fluid flux would be significantly smaller in the infiltration 974 decarbonation model. Thus, the order-of-magnitude estimates from 975 natural observations in this study indicate that the decarbonation pro-976 cess in the subducting slab could be more intense than predicted by 977 the conventional model. In addition to the decarbonation reactions in 978 the basalt-sediment units (Gorman et al. 2006), other sources like the 979 underlying mafic-ultramafic units and/or underlying subducting rocks, 980 and other mechanisms including carbonate dissolution account for a 981 large proportion of the total CO₂ fluxes from the slab. 982

9.6. Fate and residence time of carbonate in the fluid

Our data and estimates indicate that a large amount of carbonate- 984 bearing fluid flowed during eclogite-facies metamorphism of Alpine 985 Corsica. A proportion of these fluids may have reprecipitated carbonate 986 minerals and other minerals at HP conditions (Piccoli et al., 2016) or 987 have been consumed in retrograde reactions, whereas the rest was ulti-988 mately released to shallower reservoirs (Kelemen and Manning, 2015). 989 The carbonate-bearing metamorphic crack-seals represent direct 990 evidence for the reprecipitation of C-bearing fluids at HP conditions. 991 The Ar-Ar dates of phengite from the carbonate-bearing eclogitic 992 crack-seals yield minimum ages of about 29 Ma for this precipitation. 993 This age is about 5 Ma younger than the eclogite-facies metamorphic 994 peak for these rocks (34 Ma). Interestingly, eclogite veins from New 995 Caledonia have been recently shown to have formed about 6 Ma later 996 than the regional peak metamorphic conditions, and under very fast 997 precipitation conditions (Taetz et al., 2018). These similar patterns 998 suggest similar subduction/exhumation rates for the two fossil subduc- 999 tion systems and a common mechanism of fluid circulation and vein 1000 formation during the early decompression history of HP rocks. Further- 1001 more, one of the two Corsica samples yields much younger ages of about 1002 25 Ma (about 9 Ma younger than the age of peak metamorphism). This 1003 suggests that the C-bearing fluid remained within the slab for a long 1004 time span, although the peak metamorphic T of the rocks slightly 1005 exceeds the expected closure T for Ar-Ar (ca. 450 °C). Even though 1006 these veins contain very well preserved HP assemblages and mineral 1007 composition, the dates possibly represent the cooling ages rather 1008 than the crystallization ages. Nevertheless, these crack-seals contain 1009 typical HP assemblages, demonstrating that the reprecipitation of car- 1010 bonates occurred at metamorphic conditions close the reconstructed 1011 decarbonation/dissolution processes. Other evidence for metamorphic 1012 reprecipitation of carbonate has been documented in Corsica. Intense 1013 metamorphic carbonation has been recently reported in the eclogitic 1014 units of Corsica in rocks of the metabasaltic suite (Piccoli et al., 2016), 1015 and may possibly testify for the migration of these carbonic fluids 1016 within the slab. 1017

Experimental studies (Caciagli and Manning, 2003) and field obser-Q23 vations (Ague and Nicolescu, 2014) indicate that carbonate dissolves 1019 in water congruently. In our case, this would imply that a fair amount 1020 of Ca is also released from pillow basalts during metamorphism and 1021 can interact with the surrounding lithologies. Part of this Ca was bound in silicates such as the newly-formed garnet. 1023

10. Conclusion

Dehydration, decarbonation and carbonate dissolution accompany 1025 subduction of oceanic crustal sequences and release large amounts of 1026 C-O-H-bearing fluids. The exceptional lawsonite-eclogite facies rocks 1027 of Corsica provide insights into the interplay between these processes 1028 and their contributions to the C budget in subducting slabs. The studied 1029

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1030 samples indicate that structures and mineral assemblages inherited 1031 from seafloor hydrothermal alteration play an important role in the localization of important fluid-rock processes at HP conditions. Primary 1032 1033 hydrothermal structures concentrating high amounts of carbonates may act as the preferential sites for fluid localization and fluid-rock interac-1034 tions. Our data indicate that coupled hydration and decarbonation/ 1035 dehydration processes driven by upward, up-T fluid flow are responsible 1036 for the release of significant amounts of carbonic fluids during prograde 1037 1038 metamorphism. The calculated amount of CO₂ released by these reactions in the natural samples (20–70 kg per m³ of reacted rock) is 1039 consistent with (or higher than) the estimates for decarbonation of 1040 metabasalts under open system behavior at comparable depths (17 kg 1041 per m³). Conversely, the calculated time-integrated CO₂ fluxes through 1042 the upper part of the subducted oceanic crust are potentially much 1043 greater than previously proposed cumulative fluxes that are generated 1044 throughout slab sections. The Corsican rocks indicate that only a portion 1045 of these fluids was released from the slab, whereas the rest was involved 1046 in successive intra-slab fluid-rock interactions leading to partial carbon-1047 ate precipitation and decrease of dissolved carbon. Further effort will be 1048 necessary to integrate these data into a coherent model of fluid flow and 1049 fluxes through a complete section of subducting oceanic lithosphere. 1050

1051 Supplementary data to this article can be found online at https://doi. 1052 org/10.1016/j.lithos.2018.01.028.

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References 1067

- 1068 Ague, J.J., 1998. Simple models of coupled fluid infiltration and redox reactions in the 1069 crust. Contributions to Mineralogy and Petrology 132, 180-197.
- 1070 Ague, J.J., 2014. Fluid flow in the deep crust. In: Holland, H.D., Turekian, K.K. (Eds.),
- 1071 Treatise on Geochemistry. Geological Society of America, pp. 203-247. 1072 Ague, J.J., Carlson, W.D., 2013. Metamorphism as garnet sees it: the kinetics of nucleation
- 1073 and growth, equilibration, and diffusional relaxation. Elements 9, 439-445.
- 1074 Ague, J.J., Nicolescu, S., 2014. Carbon dioxide released from subduction zones by fluid-1075 mediated reactions. Nature Geoscience 7, 355-360.
- 1076 Alt, J.C., 1995. Subseafloor Processes in Mid-Ocean Ridge Hydrothermal Systems, Das P-T-X_{CO2} Stabilitätsfeld Von Lawsonit. American Geophysical Union, Washington, DC. 1077
- Q27 Alt, J.C., Teagle, D., 1999. The uptake of carbon during alteration of ocean crust. 1079 Geochimica et Cosmochimica Acta.
- Alt, J.C., Muehlenbachs, K., Honnorez, J., 1986. An oxygen isotopic profile through the Q28
- 1081 upper kilometer of the oceanic crust, DSDP Hole 504B. Earth and Planetary Science 1082 Letters 1083 Balashov, V.N., Yardley, B., 1998. Modeling metamorphic fluid flow with reaction-
- 1084 compaction permeability feedbacks. American Journal of Science 298, 441–470. Q29
- Ballèvre, M., Pitra, P., Bohn, M., 2003. Lawsonite growth in the epidote blueschists from 1086 the Ile de Groix (Armorican Massif, France): a potential geobarometer, Journal of Metamorphic Geology. 1087
- Baumgartner, L.P., Ferry, J.M., 1991. A model for coupled fluid-flow and mixed-volatile 1088 mineral reactions with applications to regional metamorphism. Contributions to 1089 1090 Mineralogy and Petrology 106, 270-285.
- 1091 Beltrando, M., Manatschal, G., Mohn, G., Dal Piaz, G., Vitale Brovarone, A., Masini, E., 2014. 1092 Recognizing remnants of magma-poor rifted margins in high-pressure orogenic 1093 belts: the Alpine case study. Earth Science Reviews 131, 88-115.
- Brunet, C., Monié, P., Jolivet, L., Cadet, J.P., 2000. Migration of compression and extension in the Tyrrhenian Sea, insights from ⁴⁰Ar/³⁹Ar ages on micas along a transect from 1094 1095 Corsica to Tuscany. Tectonophysics 321, 127-155. 1096
- 1097 Caron, J.M., Delcey, R., 1979. Lithostratigraphie des schistes lustrés corses: diversité des séries
- 1098 post-ophiolitiques. Comptes Rendus de l'Académie des Sciences 208, 1525-1528.

Caron, J.M., Péquignot, G., 1986. The transition between blue-schist and lawsonite bearing	1099
eclogites on the example of Corsican metabasalt. Lithos 19, 205–218.	1100
in melt and cordierite: implications for dehydration, partial melting and graphite pre-	1102
cipitation. Journal of Metamorphic Geology 31, 843-862.	1103
Clarke, G.L., Powell, R., Fitzherbert, J.A., 2006. The lawsonite paradox: a comparison of	1104
field evidence and mineral equilibria modelling. Journal of Metamorphic Geology 24, 715–725	1105
Collins, N.C., Bebout, G.E., Angiboust, S., Agard, P., Scambelluri, M., Crispini, L, John, T., 2015.	1107
Subduction zone metamorphic pathway for deep carbon cycling: II. Evidence from	1108
HP/UHP metabasaltic rocks and ophicarbonates. Chemical Geology 412, 132–150.	1109
COOK-KOIIARS, J., BEDOUE, G.E., COIIINS, N.C., ANGIDOUSE, S., 2014. SUDDUCTION ZONE METAMOR-	Q30
rocks, Italian alps. Chemical Geology.	1112
Donohue, C.L., Essene, E.J., 2000. An oxygen barometer with the assemblage garnet-	1113
epidote. Earth and Planetary Science Letters 181, 459–472.	1114
Faccenda, M., 2014. Water in the slad: a trilogy. Jectonophysics 614, 1–30. Ferrando S. Gronno C. Frezzotti MJ. Castelli D. Prover A. 2017. Dissolving dolomite	1110
in a stable UHP mineral assemblage: evidence from Cal-Dol marbles of the Dora-	1117
Maira Massif (Italian Western Alps). American Mineralogist 102, 42-60.	1118
Frezzotti, M.L., Selverstone, J., Sharp, Z.D., Compagnoni, R., 2011. Carbonate dissolution	1119
4 703–706	1120
Gillis, K.M., Coogan, L.A., 2011. Earth and Planetary Science Letters 302, 385–392.	1122
Gonzalez, C.M., Gorczyk, W., Gerya, T.V., 2016. Decarbonation of subducting slabs: insight	1123
from petrological-thermomechanical modeling, Gondwana Research 36, 314–332.	1124
decarbonation of subducting slabs. Geochemistry, Geophysics, Geosystems 7, 1–21.	1126
Greenwood, H.J., 1975. Buffering of pore fluids by metamorphic reactions. American	1127
Journal of Science 275, 573–593.	1128
Himalava (Ladakh, NW India): exploring the complex behavior of a lawsonite-	1130
bearing system in a paleo-accretionary setting. Lithos 252-253, 41–56.	1131
Guevara, V.E., Caddick, M.J., 2016. Shooting at a moving target: phase equilibria modelling	1132
of high-temperature metamorphism. Journal of Metamorphic Geology 34, 209–235.	1133
constraints on carbon recycling and storage in the mantle. Earth and Planetary	1135
Science Letters 214, 357–368.	1136
Healy, D., Reddy, S.M., Timms, N.E., Gray, E.M., Vitale Brovarone, A., 2009. Earth and Plan-	1137
Holland TTR Powell R 1998 An internally consistent interest thermodynamic data set	1130
for phases of petrological interest. Journal of Metamorphic Geology 16, 309–343.	Q31
Holland, T.J.B., Powell, R., 2003. Activity-composition relations for phases in petrological	1141
calculations: an asymmetric multicomponent formulation. Contributions to Mineralogy	1142
Jarrard. R.D., 2003. Subduction fluxes of water, carbon dioxide, chlorine, and potassium.	1143
Geochemistry, Geophysics, Geosystems 4.	1145
Jolivet, L., Faccenna, C., Goff, E.B., Mattei, M., Rossetti, F., Brunet, C., Storti, F., Funiciello, R., Cadet,	1146
P., Agostino, N., Parta, I., 1998. Midcrustal snear zones in postorogenic extension: example from the northern Tyrrhenian Sea. Journal of Geochemical Exploration 103	1147
Kelemen, P.B., Manning, C.E., 2015. Reevaluating carbon fluxes in subduction zones, what	1149
goes down, mostly comes up. Presented at the Proceedings of the National Academy	1150
of Sciences.	1151
metabasalts: implications for seismicity, arc magmatism and volatile recycling.	1153
Earth and Planetary Science Letters 189, 19–29.	1154
Keshav, S., Gudfinnsson, G.H., 2010. Experimentally dictated stability of carbonated	1155
oceanic crust to moderately great depths in the Earth; results from the solidus deter- mination in the system $CaO-MgO-Al_{2}O_{2}-SiO_{2}-CO_{2}$. Journal of Geophysical Research	1150
115, B05205.	1158
Lagabrielle, Y., Lemoine, M., 1997. Alpine, Corsican and Apennine ophiolites: the slow-	1159
spreading ridge model. Comptes Rendus de l"Acad"emie des Sciences 325, 909–920.	1160
Science Reviews 141. 1–26.	Q32
Lahondère, D., Guerrot, C., 1997. Datation Nd-Sm du métamorphisme éclogitique en Corse	1163
alpine: un argument pour l'existence, au Crétacé supérieur, d'une zone de subduc-	1164
tion active localisee ie long du block corse-sarde. Geologie de la France 3, 3–11. Li LL Klemd R. Gao I. Meyer M. 2012 Coexisting carbonate-bearing eclogite and	1165
blueschist in SW Tianshan, China: petrology and phase equilibria. Journal of Asian	1167
Earth Sciences 60, 174–187.	1168
Li, J.L., Klemd, R., Gao, J., Meyer, M., 2014. Compositional zoning in dolomite from	1169
nhism during subduction of oceanic crust American Mineralogist 99, 206–217	1170
Malavieille, J., Chemenda, A., Larroque, C., 1998. Evolutionary model for Alpine Corsica:	1172
mechanism for ophiolite emplacement and exhumation of high-pressure rocks.	1173
Terra Nova 10, 317–322. Malusà M.C. Eaconna C. Baldwin, S.L. Eitzgenald, B.C. Beccetti, E. Balestrieri, M.L.	1174
Danišík, M., Ellero, A., Ottria, G., Piromallo. C. 2015. Contrasting styles of (U)HP	1176
rock exhumation along the Cenozoic Adria-Europe plate boundary (Western Alps,	1177
Calabria, Corsica). Geochemistry, Geophysics, Geosystems 16, 1786–1824.	1178
NIATION, N., FANGOIN, L., 2003. DEFORMATION HISTORY OF the ophiolite sequence from the Balagne Nappe, northern Corsica: insights in the tectonic evolution of Alpine Corsica.	1180
Coological Journal 38, 67–83	1121

Martin, L.A.L. Rubatto, D., Vitale Brovarone, A., Hermann, L. 2011, Late Eocene lawsonite-1182 eclogite facies metasomatism of a granulite sliver associated to ophiolites in Alpine 1183 Corsica, Lithos 125, 620-640. 1184

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Meresse, F., Lagabrielle, Y., Malavieille, J., Ildefonse, B., 2012. Tectonophysics. Tectonophysics 579, 4–16.

- Miller, J.A., Cartwright, I., 2006. Albite vein formation during exhumation of high-pressure terranes: a case study from alpine Corsica. Journal of Metamorphic Geology 24, 409–428.
- Miller, J.A., Buick, I.S., Cartwright, I., 2000. Textural implications of high-pressure fluid flow controlled by pre-subduction deformation and alteration patterns. Journal of Geochemical Exploration 69-70, 551–555.
- Miller, J.A., Cartwright, I., Buick, I.S., Barnicoat, A.C., 2001. An O-isotope profile through the HP-LT Corsican ophiolite, France and its implications for fluid flow during subduction. Chemical Geology 178, 43–69.
- Molina, J.F., Poli, S., Austrheim, H.K., Glodny, J., Rusin, A., 2004. Eclogite-facies vein systems in the Marun-Keu complex (Polar Urals, Russia): textural, chemical and thermal constraints for patterns of fluid flow in the lower crust. Contributions to Mineralogy and Petrology 147, 484–504.
- Pattison, D.R.M., de Capitani, C., GAIDIES, F., 2011. Petrological consequences of variations in metamorphic reaction affinity. Journal of Metamorphic Geology 29, 953–977.
- Piccoli, F., Vitale Brovarone, A., Beyssac, O., Martinez, I., Ague, J.J., Chaduteau, C., 2016.
 Carbonation by fluid-rock interactions at high-pressure conditions: implications for carbon cycling in subduction zones. Earth and Planetary Science Letters 445, 146–159.
- Plümper, O., John, T., Podladchikov, Y.Y., Vrijmoed, J.C., Scambelluri, M., 2016. Fluid escape
 from subduction zones controlled by channel-forming reactive porosity. Nature
 Geoscience 10, 150–156.
- Poli, S., 2015. Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. Nature Geoscience 8, 633–636.
- Poli, S., Franzolin, E., Fumagalli, P., Crottini, A., 2009. The transport of carbon and hydrogen in subducted oceanic crust: an experimental study to 5 GPa. Earth and Planetary Science Letters 278, 350–360.
- Ravna, E.J.K., Andersen, T.B., Jolivet, L., de Capitani, C., 2010. Cold subduction and the
 formation of lawsonite eclogite constraints from prograde evolution of eclogitized
 pillow lava from Corsica. 28, 381–395.
- Rossi, P., Cocherie, A., Lahondère, D., Fanning, C.M., 2002. La marge européenne de la
 Téthys jurassique en Corse: datation de trondhjémites de Balagne et indices de croîte
 continentale sous le domaine Balano-Ligure. Comptes Rendus Geoscience 334,
 313-322.
- Rubatto, D., Gebauer, D., Compagnoni, R., 1999. Dating of eclogite-facies zircons: the age of
 Alpine metamorphism in the Sesia–Lanzo Zone (Western Alps). Earth and Planetary
 Science 167, 141–158.
- Scambelluri, M., Bebout, G.E., Belmonte, D., Gilio, M., Campomenosi, N., Collins, N.,
 Crispini, L., 2016. Earth and Planetary Science Letters 441, 155–166.
- Staudigel, H., 2003. Hydrothermal alteration processes in the oceanic crust. Treatise on Geochemistry 3, 511–535.
- Staudigel, H., 2014. 4.16 Chemical fluxes from hydrothermal alteration of the oceanic crust. The Crust, 2nd ed. Elsevier Ltd.
- Staudigel, H., Hart, S.R., Schmincke, H.U., Smith, B.M., 1989. Cretaceous ocean crust at DSDP Sites 417 and 418: carbon uptake from weathering versus loss by magmatic outgassing. Geochimica et Cosmochimica Acta 53, 3091–3094.

- Staudigel, H., Plank, T., White, W.M., Schmincke, H.U., 1996. Geochemical fluxes during seafloor alteration of the upper oceanic crust: DSDP Sites 417 and 418. In: Bebout, 1233
 G.E., Scholl, D.W., Kirby, S.H., Platt, J.P. (Eds.), SUBCON: Subduction From Top to Bottom. AGU Geophysical Monograph, pp. 19–38. 1235
- Stüwe, K., 1997. Effective bulk composition changes due to cooling: a model predicting complexities in retrograde reaction textures. Contributions to Mineralogy and Petrology 129, 43–52.
 1236
- Syracuse, E.M., van Keken, P.E., Abers, G.A., 2010. The global range of subduction zone thermal models. Physics of the Earth and Planetary Interiors 183, 73–90.
 Taetz, S., John, T., Bröcker, M., Spandler, C., Stracke, A., 2018. Fast intraslab fluid-flow 1241
- Taetz, S., John, T., Bröcker, M., Spandler, C., Stracke, A., 2018. Fast intraslab fluid-flow 1241 events linked to pulses of high pore fluid pressure at the subducted plate interface. 1242 Earth and Planetary Science Letters 482, 33–43. 1243
- Tsujimori, T., Ernst, W.G., 2014. Lawsonite blueschists and lawsonite eclogites as proxies
 for palaeo-subduction zone processes: a review. Journal of Metamorphic Geology
 32, 437-454.
- van Keken, P.E., Hacker, B.R., Syracuse, E.M., Abers, G.A., 2011. Subduction factory: 4. 1247
 Depth-dependent flux of H₂O from subducting slabs worldwide. Journal of Geophysical Research 116, B01401. 1249
- Vitale Brovarone, A., Beyssac, O., 2014. Lawsonite metasomatism: a new route for water to the deep Earth. Earth and Planetary Science Letters 393, 275–284. 1251
- Vitale Brovarone, A., Herwartz, D., 2013. Timing of HP metamorphism in the Schistes Lustrés of Alpine Corsica: new Lu-Hf garnet and lawsonite ages. Lithos 172-173, 1253 175-191. 1254
- Vitale Brovarone, A., Beltrando, M., Malavieille, J., Giuntoli, F., Tondella, E., Groppo, C., 1255
 Beyssac, O., Compagnoni, R., 2011a. Inherited Ocean–Continent Transition zones in deeply subducted terranes: insights from Alpine Corsica. Lithos 124, 273–290.
 1257
- Vitale Brovarone, A., Groppo, C., Hetényi, G., Compagnoni, R., Malavieille, J., 2011b. 1258
 Coexistence of lawsonite-bearing eclogite and blueschist: phase equilibria modelling of Alpine Corsica metabasalts and petrological evolution of subducting slabs. Journal of Metamorphic Geology 29, 583–600. 1261
- Vitale Brovarone, A., Beyssac, O., Malavieille, J., Molli, G., Beltrando, M., Compagnoni, R., 2013. Stacking and metamorphism of continuous segments of subducted lithosphere in a high-pressure wedge: the example of Alpine Corsica (France). Earth Science Reviews 116, 35–56.
 1263
- Vitale Brovarone, A., Picatto, M., Beyssac, O., Lagabrielle, Y., 2014. The blueschist–eclogite transition in the Alpine chain: P–T paths and the role of slow-spreading extensional structures in the evolution of HP–LT mountain belts. Tectonophysics 615-616, 1268 96–121.
 1269
- Wada, I., Behn, M.D., Shaw, A.M., 2012. Earth and Planetary Science Letters 353-354, 1270 60-71. 1271
- Wark, D.A., Watson, B., 2002. Grain-scale channelization of pores due to gradients in temperature or composition of intergranular fluid or melt. Journal of Geophysical Research 107 (5–1–15).
 1274
- White, R.W., Powell, R., Holland, T.J.B., 2007. Progress relating to calculation of partial 1275 melting equilibria for metapelites. Journal of Metamorphic Geology 25, 511–527.
 1276
- Zack, T., John, T., 2007. An evaluation of reactive fluid flow and trace element mobility in subducting slabs. Chemical Geology 239, 199–216. 1278