Fluid-mediated selective dissolution of subducting carbonaceous material: implications for carbon recycling and fluid fluxes at forearc depths

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Abstract

Subduction of crustal C governs the long-term global C cycling. The role of carbonates recycling in subduction zones and the related dissolution of C at various depths have been the subject of a large body of literature over the last decades. Much less is known about the contribution of carbonaceous material (CM) to the deep C cycling in subduction zones. This paper presents natural evidence for intense fluid-mediated leaching of CM in pelitic schists at high-pressure/low-temperature conditions relevant to the forearc region of subducting slabs. Manifestations of such process were identified along fluid pathways at various scales in the blueschist-facies subduction complexes of both Alpine Corsica and the Western Alps. Microstructural, whole-rock and Raman analyses across a selected metasomatic aureole were used to quantify the amount and mechanisms of C loss during fluid-rock interaction. In samples affected by intense fluid infiltration, more than 90% of the initial CM was removed from the rock. Microstructural and micro-Raman data indicate selective leaching of disordered CM relative to nearly crystalline graphite. The collected data allowed constraining the magnitude of fluid fluxes required to bleach the studied CM-bearing lithologies at different P-T-\(O_2\) conditions, which corresponds to rather high time-integrated fluid fluxes in the order of \(\sim 10^6\) m\(^3\)/m\(^2\). In settings of large-scale fluid channelization, such as along regional-scale, lithological/tectonic boundaries or at the top of the subducted sedimentary pile, intense dissolution of subducted CM is expected. This process may thus exert a negative feedback on the sink of C phases into the deep mantle over the geological timescales and contribute to the release of isotopically light C from subducting slabs in forearc regions.
1. Introduction

Subduction of crustal C plays a central role in the global C cycle. Carbonate mineral and carbonaceous material (CM) are the main reservoirs of C in subducting slabs (Hayes and Waldbauer, 2006; Plank, 2014). Metamorphism of carbonate minerals, through either decarbonation/melting reactions or dissolution, has been the focus of considerable research over the last decades (Ague and Nicolescu, 2014; Cook-Kollars et al., 2014; Facq et al., 2014; Gorman et al., 2006; Kelemen and Manning, 2015; Poli, 2015). The contribution of carbonaceous material (CM) to deep C fluxes is less well known, despite the fact that CM is the main input of organic C to subduction zones (Hayes and Waldbauer, 2006; Plank, 2014).

With rising temperature during subduction, CM is progressively transformed into graphite through a series of intermediate stages of disordered graphitic C (Buseck and Beyssac, 2014). The progressive transformation of CM into graphite results in loss of heteroatoms such as O, H, and N, as well as some C. Release of C during the earliest transformations of subducted carbonaceous material (< 300 °C) is well established and results in the release of C compounds including thermogenic hydrocarbons and CO₂ (Mullis et al., 1994; Tarantola et al., 2007). At higher metamorphic grades, the behavior of CM is generally considered less mobile than carbonate minerals. Owing to its high buffering potential in oxidized geological fluids (Duncan and Dasgupta, 2017; Hermann et al., 2006), graphitic C, especially crystalline graphite, may be largely retained in the rock even at high temperature conditions. For example, CM is dominantly retained in sedimentary rocks heated by contact metamorphism to temperatures of 600 °C or more (Pattison, 2006). At similar temperature but higher pressure conditions, dissolution of CM is documented during regional Barrovian-style metamorphism of the Wepawaug Schist, Connecticut, USA (Zhang et al., 2018). In this case, a loss of about 26% of the bulk rock CM content was observed in kyanite-bearing metapelites (~ 600°C) with respect to lower-grade chlorite-biotite zone precursors. In subduction zones, analysis of sedimentary rocks metamorphosed under closed system conditions suggests that more than 75% of the initial subducted CM is preserved down to depths of ~100 km (Cook-Kollars et al., 2014).

However, the behavior of subducted CM in open system conditions, e.g. along fluid percolation pathways, is less constrained. Most studies focusing on the behavior of reduced C in open systems have dealt with graphite deposition (Duke and Rumble, 1986; Evans et al., 2002; Galvez et al., 2013; Luque et al., 2009; Vitale Brovarone et al., 2017), whereas fluid-mediated removal of CM is still scarcely documented (Mori et al., 2014). In particular, fluid-rock interactions along channelized fluid pathways may strongly affect the stability of C-bearing phases, as shown for carbonate minerals through processes of decarbonation (Gorman et al., 2006), fluid-mediated carbonate dissolution (Ague and Nicolescu, 2014), or carbonation (Piccoli et al., 2016). Under these circumstances, the conditions suitable for CM mobilization (Tumiati and Malaspina, 2019; Tumiati et al., 2017) may be enhanced relative to closed
In particular, although the solubility of CM may be low in aqueous fluids, protracted and/or repeated infiltration of aqueous fluids into CM-bearing lithologies has the potential to progressively remove organic C from the rock.

In this contribution, we document natural evidence for fluid-mediated dissolution of CM in metasedimentary rocks at blueschist-facies, high-pressure/low-temperature (HP/LT) conditions within the Schistes Lustrés complex of Alpine Corsica and Western Alps. After a general presentation of the characteristic rocks and microstructures, detailed mineralogical and geochemical data is be presented for a selected metasomatic aureole from Alpine Corsica. Microstructural data, bulk CM concentrations, Raman spectroscopy, and thermodynamic calculations are integrated to describe the patterns of fluid rock interactions and dissolution of CM, to estimate the time-integrated fluid fluxes along channeled fluid pathways in the subducting slab at forearc depths, and to examine the related geochemical implications.

2. Geologic setting

The Schistes Lustrés complex of Alpine Corsica and Western Alps (Fig. 1) mainly consists of Tethyan oceanic/transitional metaophiolitic rocks and associated metasedimentary cover rocks units that were variably transformed in the Alpine subduction system (Agard et al., 2001; 2002; Beltrando et al., 2010; Elter, 1971; Lagabrielle et al., 2015). In both belts, these units underwent high-pressure/low-temperature (HP/LT) metamorphism ranging from low-grade to lawsonite eclogite-facies conditions (Agard et al., 2009; Angiboust et al., 2009; Fournier et al., 1991; Groppo and Castelli, 2010; Ravna et al., 2010; Schwartz et al., 2013; Vitale Brovarone et al., 2013).

This study centers on the blueschist-facies domain of the Schistes Lustrés complex exposed in Alpine Corsica and Western Alps (Fig. 1). In both belts, this terrane consists mostly of large metasedimentary suites containing variable proportions of CM-rich metapelitic schists and marble layers that incorporate blocks and slices of mafic and ultramafic rocks such as metagabbros, metabasalts, and serpentinites (Balestro et al., 2015; Lagabrielle et al., 2015; Lagabrielle and Lemoine, 1997; Lemoine, 2003; Polino and Lemoine, 1984; Vitale Brovarone et al., 2014b). These suites are exposed within a rather continuous metamorphic gradient from ~ 300 °C and P < 1 GPa to ~ 480 °C and 1.8 GPa (Agard et al., 2009; Gabalda et al., 2009; Schwartz et al., 2013; Vitale Brovarone et al., 2014b) (Fig. 1b).

In the investigated blueschist-facies units, whole rock carbon budgets in metasedimentary rocks unaffected by substantial fluid percolation show a general preservation of the initial marine carbonate and organic C concentrations and C stable isotope signature, pointing to little carbon mobilization during prograde metamorphism (Cartwright and Buick, 2000; Cook-Kollars et al., 2014). In this study we focus on channelized fluid pathways localized along the contacts.

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separating mafic/ultramafic blocks and slices from the enclosing metasedimentary rocks. Previous work has documented the presence of fluid-mediated metasomatic halos along these contacts in the blueschist-facies units of Alpine Corsica. In particular, it has been shown that the metasedimentary rocks in contact with mafic/ultramafic rocks are characterized by the precipitation of metasomatic lawsonite (Vitale Brovarone et al., 2014a; Vitale Brovarone and Beyssac, 2014).

Figure 1
Metamorphic maps of the study areas in Alpine Corsica (a) and Western Alps (b), modified after Vitale Brovarone, Picatto et al. (2014) and Schwartz et al., (2013), respectively. Estimated peak conditions based on Raman Spectroscopy of Carbonaceous Material and thermodynamics are also shown. In Alpine Corsica, the lower-grade T appearance of CM leaching in metasomatic aureoles corresponds to the field-based isograd for lawsonite metasomatism (~ 370 °C), while in the Western Alps, similar processes were found at lower T in the range of 330-340 °C.
Equivalent processes are described in this work for in the equivalent blueschist-facies units of
the W. Alps (Fig. 1b). In Alpine Corsica, this phenomenon was observed from minimum T
conditions of about 370 °C and corresponding P of ~ 1-1.3 GPa up to the boundary with the
underlying eclogite-facies unit at ~ 480 °C and 1.8 GPa (Fig. 1). No evidence for fluid-rock
interactions and metasomatism was found within the same lithological suite at lower T in
Alpine Corsica, and the T of ~ 370 °C was proposed as a regional-scale isograd for this process
(Vitale Brovarone et al., 2014a). In the blueschist units of the Western Alps, evidence for this
process was found from slightly lower T conditions of ~ 340 °C (Fig. 1). Owing to the more
intense retrograde overprint and lawsonite breakdown in the Western Alps units compared to
Alpine Corsica, only overprinted lawsonite metasomatic aureoles were identified at T > 400 °C
(Fig. 1).

3. Methods

3.1. Sample collection and preparation

Rock samples were collected in the areas shown in Figure 1, which also presents the distribution
of more than 230 outcrops identified in the two belts: > 200 outcrops in Alpine Corsica, part of
which was already presented in Vitale Brovarone et al., 2014a, and 32 in the Western Alps
(stars refer to main localities). About 80 samples from the two belts were selected for thin
section preparation. Fourteen samples were collected from one selected reaction zone in Alpine
Corsica (location in Fig. 1a) for detailed geochemical and Raman spectroscopy study. The
samples were then cut to remove surface weathering. One chip of approximately 4x4x4 cm was
isolated for each sample and cut into two parts for thin section preparation and bulk rock
analysis, respectively. For bulk rock analysis, the samples were crushed and then pulverized
with an agate mortar.

3.2. Bulk-rock C and trace element concentrations

Whole-rock analyses were performed at the Service d’Analyse des Roches et Minéraux
(SARM, Centre de Recherches Pétrographiques et Géochimiques, Nancy, France). Total CO2
concentration was analyzed using a LECO SC 144DRPC analyzer (LECO France, Garges les
Gonesse, France) through calcination at 1400 °C. The uncertainty on the total CO2 content is
<10% for contents between 0.5 and 1%, <20% for contents between 0.5% and 0.1%, and >20%
for contents <0.1% (detection limit 0.01%). Total organic C was analyzed following the same
protocol after removal of all carbonates. The uncertainty on the total organic C (Corg) content
is <15% for contents between 0.5 and 0.1% and >15% for contents <0.1% (detection limit
0.01%). The bulk inorganic C (carbonate minerals) content in the samples was calculated by
subtracting the organic C from the total C. The results are presented in Table 1. The major and
trace element analyses were done by alkali fusion of rock samples (LiBO$_2$), followed by concentration measurements using an ICP-OES Icap 6500 (Thermoscientific) for major elements, and an ICP-MS X7 (Thermoscientific) for trace elements (protocol by Carignan et al., 2001). The uncertainty on the elements used for mass balance calculations (see Section 5.2) are Hf: <10%, Th: <10%, and Zr: >5%.

3.3. Microscopic observations and Raman spectroscopy

Microstructural and petrographic characterizations were carried out on petrographic thin sections with an optical microscope first, and then by scanning electron microscopy (SEM). Petrographic thin sections were carbon coated for SEM work. Observations were performed at a working distance of 7.5 mm using a Zeiss Ultra 55 field emission gun SEM operated at 15 kV with a 120 μm aperture. Backscattered electron (BSE) mode was used to investigate chemical heterogeneities using an Angle Selective Backscattered Detector (AsB) or an Energy Selective Backscattered Detector (EsB).

Raman spectra were obtained using a Renishaw InVIA Reflex microspectrometer (IMPMC Paris). We used a 514 nm MODULASER argon laser in circular polarization. The laser was focused on the sample by a DMLM Leica microscope with a 100x objective (NA = 0.85), and the laser power at the sample surface was set around 1 mW. The Rayleigh diffusion was eliminated by edge filters, and to achieve a nearly confocal configuration, the entrance slit was closed down to 15 μm. The signal was finally dispersed using a 1,800 gr/mm grating and analyzed by a Peltier cooled RENCAM CCD detector. Before each session, the spectrometer was calibrated with a silicon standard. Because Raman spectroscopy of CM can be affected by several analytical mismatches, we followed closely the analytical and fitting procedures described by Beyssac et al. (Beyssac et al., 2002; 2003a). Measurements were taken on polished thin sections cut perpendicularly to the main fabrics, and CM was systematically analyzed below a transparent adjacent/including mineral. The spectra were recorded in the extended scanning mode (700–2,000 cm$^{-1}$) with acquisition times from 30 to 60 s. The number of spectra for each sample is reported in Figure 3. Spectra were then processed using the software Peakfit (Beyssac et al., 2002). The Raman results, expressed as R2 values (see Section 4.2 for details), are presented in Table 2.

3.4. Thermodynamic modeling

Thermodynamic modeling was used to estimate the solubility of CM at the considered metamorphic conditions and to assess the amount of aqueous fluid required to mobilize CM in the selected samples (Section 5.4). Molar fractions of H$_2$O, CO$_2$ and CH$_4$ in equilibrium with two types of CM for which thermodynamic data are available at the considered metamorphic
conditions (Tumiati et al., 2020): an X-ray amorphous, glass-like C (Alpha Aesar, type I; hereafter glass-like C), and crystalline graphite. Based on the thermodynamic data of Tumiati et al. (2020), glass-like C has higher Gibbs free energy compared to graphite at P below around 3 GPa (T playing a minor effect), and consequently higher solubility. For this reason, these two types of CM were considered as reference for higher (glass-like C) and lower (graphite) CM solubility in aqueous fluids at the considered conditions. P–T conditions of 1.0 GPa–300°C, 1.3 GPa–370°C and 1.7 GPa–425°C — consistent with the regional, W-E metamorphic gradient in the considered terranes (Fig. 1) — were considered. The thermodynamic properties of glass-like C and graphite at the considered conditions have been retrieved using the graphite-saturated COH fluid EoS by Connolly and Cesare (1995) and the routine "fluids" of the Perple_X package (Connolly, 1995). The CM in the model was considered to be chemically pure, with no heteroatoms such as N, S, and H. For each calculation, the fO₂ was buffered at conditions corresponding to the maximum activity of water (H₂O-maximum hereafter) The calculations were done at C saturation conditions owing to the presence of at least some CM throughout the reaction zones (Section 4.1). A rock density of 2.7 g/cm³ was considered for the modeled metapelites. The augmented Gibbs free energy of formation of glass-like C has been modeled by setting the activity of C [a(C)] in the calculations to values > 1 (Connolly, 1995). The moles of C dissolved in COH fluids, in equilibrium either with graphite or glass-like C, have then been compared with the moles of C leached out from the rocks (averaged to 67.5 mol/m³ rock, corresponding to 0.03 wt.% graphite, see Section 4.1), yielding the amount of fluid (m³) required to complete the dissolution process. The calculated fluid component speciations are presented in Table 4.

4. RESULTS

4.1. Field and sample description

All collected samples exhibit a marked schistosity parallel to the contact with the mafic/ultramafic blocks. Next to the contact zone, the rocks show a marked bleaching of the metasediments. The thickness of the bleached aureole ranges from a few tens of cm to several meters and systematically matches with the precipitation of lawsonite. As a general feature, the bigger the mafic/ultramafic block, the thicker the metasomatic halo (Vitale Brovarone et al., 2014a). Several examples of these metasomatic rinds can be observed along the road joining Bocca a Serna and Morosaglia in Alpine Corsica (bottom part of the map in Fig. 1a). In the area of Colle dell’Agnello, Western Alps (Fig. 1b), the intersection between metasomatic aureoles rimming large mafic bodies and the topography locally defines large surfaces (tens of m) exposing the lawsonite-bearing, bleached rocks studied here (Fig. 3).
The general appearance of the bleached rocks is remarkably similar in the two belts (Figs. 2-4). A characteristic feature of the studied rocks is the presence of dark, CM-rich lawsonite crystals dispersed in a light-colored matrix mainly consisting of lawsonite + quartz + mica ± chlorite (Fig. 4). Rocks showing these features were found only in the proximity of the above-mentioned lithological boundary, or, to a lesser extent, along thin (3-5 cm thick), foliation-parallel veins within the regional metapelitic schists (Fig. 2d-f).

Figure 2

(a-c) Examples of lawsonite-bearing, CM depleted reaction zones in contact with mafic/ultramafic blocks in Alpine Corsica (See also Fig. 5 for a detailed profile). (a-a’) Example of a relatively thin reaction zone in contact with a small metagabbro block. The bleaching zone next to the contact (red line) is highlighted in (a’), which also show the distribution of CM-rich lawsonite blasts (small, elongated rectangles). The size of the blasts in not to scale). (b-c) Close-up and photomicrograph of the CM-depleted zone marked by the red box in (a’). In (c), note the presence of a CM-rich foliation preserved in the lawsonite blasts. (d-f) Example of lawsonite-bearing, CM-
depleted individual layers within the metasedimentary suite in the absence of mafic/ultramafic blocks (d-f). In (f), note the presence of CM-rich lawsonite crystals preserved in a CM-poor matrix.

Figure 3

Examples of lawsonite-bearing, CM-depleted reaction zones in contact with mafic/ultramafic rocks in the Western Alps. (a-d) General distribution and patterns of CM-leaching and lawsonite precipitation (bleached area in a’) around metabasaltic blocks (green blocks in (a’)). The size of the lawsonite blasts (small, elongated rectangles in (a’)) is not to scale. (b-d) Close-ups and photomicrograph of the CM-depleted zone marked by the red box in (a’). In (d), note the presence of a CM-rich foliation preserved in the lawsonite blasts. (e-h) General distribution and patterns of CM-leaching and lawsonite precipitation (bleached area in e’) in a complexly deformed calc-schist+metachert sequence in contact with an ultramafic block (green zone in (e’)). The size of the lawsonite blasts (small, elongated rectangles in (e’)) is not to scale, and is confined to the calc-schist layers initially present in the rock. (f-h) Close-ups and photomicrograph of the CM-depleted zone marked by the red box in (e’). In (g-h), note the presence of a CM-rich foliation preserved in the lawsonite blasts in a chlorite-lawsonite rich (g) and a quartz-carbonate-mica (h) layer.
e6 é4J6 dsaY6 b5 7Gd 3IrY6c F( 73uBGFG3a4J6C aG3aG d4Yq éIs 7u dsuh3dy6 YP 7u sx3uG6C 1 V J6dces éIs 6sq c PrY6c Gq dY6c FGdd AIC AYusx35 7G AICgad 3 36c s d4Yq éIs 7u dsuh3dy6 YP 7uY6i Gq dY6c FGdd AIC a 3us 3GY YFduhsc J6 b5 7Gd u6CJC RY6 5 J6aJ7as 6é éY s6436asc FG3a4J6C
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<th>Table 1. Bulk organic C and total CO₂ content in the selected samples across the metasomatic aureole.</th>
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<tr>
<td><strong>Sample</strong></td>
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<td><strong>Corg (wt.%)</strong></td>
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<td><strong>CO₂ (wt.%)</strong></td>
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, 4YG úa. 1 aY6ë6é 3auuí ãs us3aø6( ) Y6s dYq 6 J6 AICgus 1 Y6s øls 7uHCluddhss csau3ds J6 Yld6Je 1 7uds6ë 3d 1 V J6 øs dgcJc dB5 76Gd éYq 3ucd éls aYë6àé) Y6s 36c øls 5 J3 cu7d 3é ãs i i 36c i i Fy6Gc3udl 1 Y6s ø3éY666 Y6s d35 79G P aY66J6 ÜGü J1 Yös4u436 Yld6Je 1 q é 36c Jës7uaué 3d3uF63døs AUs3a4 ) Y6s øls 3husG cs3d6as üYl é 5 sGC3FFuYJd J6cJ3c3c R4s - j h3søs aYusd7Y6cd ëY øls J6súfbs Fs3q ss øls 5 sGC3FFuY 36c øls 5 s3ß7Géds

sd7[1s øls 5 J6súYC3dG3h3uBdY6d6[ i i aY573usc éYi i J6aagcJ6c4s PØY 3dY636c àb6dPYØ 3dY6YYPFq[ 35 74JFYG636c 73uBÇGs 7Gæs5 s6ëYPq 5Y6s ésdBJ6CéY3 aY57Gx 5 sëdY53äa shYdGdY6 ãls dscJ5 s6ëu( YudCh YBI4s i i uYad JdJ6cJ3æc F( øls uus s3u4 sG5 s6ë É22 73sðuð R4s E22 73sðuð YP6sds uYad 3us J6 BæaY66d6s6é q J4 3GYYsu 3Gürsc 36c g6Gdsúc 5 s3ß7Géds csuhiSc ) Y6d i i 36e aG3Gg ciR8u R5Y 5 øls 3cy3as6é 5 sGC3FFuY AIC B R3FG B R4s 5 sëdscJ5 s6ëu( YudCh YHI i Jd3GYY77YuS c F( øls 7uds6as YPI V J6aagcJ6d6d6 òð36[ i i J6 AIC 1 Ya3uF63s q 3dsãsãæc F( Y7d3G6c sGaaY6 5 JauYdY7( J6 øls dgcJsc dB5 76Gd J6aagcJ6C J6 øls 5 sGC3FFuY ë6 Y6s dB5 7G 4Yqshsu ãls 7uds6as YPI6( 35 Y66d YPa3uF63s JdJ6búsc F3dsc Y664s 7uds6as YP6Y8G 1T Yáuú436 1V J6 øs FgG uYa 363G3dé AIC ë6 øls 5 sGC3FFuY 6Y1V q 3dsãsãæc F( Y7d3G5s JauYdY7( 36c øls FgG uYa 1 V aY6ë6é JdJ3c3søsaY6G5 J é q é Yuo7qsu 8 R3FG dOC4G6aau3ds YPFsG ëY8G1 T Jd YP6húc J6 øls 5 sGC3FFuY ëYd ëY øls 5 sëdscJ5 sêFgë é4sFgGa Y6a6ãa6Y6u5 3Juðhss uGYq ëq é R3FG

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F 6s Qs 6s E 6s 5 Ys C 746.6a 6s 1 V q J 7s 6a 6s Ysusc 1 V 43h6c3 E h3q63 sv 3G6Y 6Y csBaæ F36c AIC 3 a AYur6bas 1 V 4s36c g6su usCY6G

3 s65 Yf 4Ja aY6cBY6ddYq6 6s PYQ j6cRE E aYur676cs6asd zl zl

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df vu

3 a Es7uds68ëths E35 36 d7saß6 BP1 V J6 6s ðgæ36d3b5 7Gd 36c aYursd7Y6c6cE h3qsd R4s csBaæF36c
d3c 6s 3dMaB6cE h3qsd csus3ds Rhys 3 ðY a E34s uaued the6q3 G 746s J6 a 43d hsus d5 3G
cF36c Bds AICus Pf 3 aY 7Gës E35 36 a43uãaðu)3dYP6 1V Rhys i ðYi B7saasg5 3 Jd
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ðs cYs J63661 V aGdsu6j6 ðs 5 3duX ðPð5 7Gd a43uãaðu) csc F cJ63667Rqgsc 5 sc33c ðð66m ðs3dY6d 36c Jd
3dY 7usds6ë6d 3d J6uQ6Q666 ð6s 7uYëGb4 5 s37sõs ð631B6csc F 5 sèKð5 3dd5 2x35 7Gd ðP5 JauYsagañug6G
cJ63667B66 1 V cJ63667B66 1 V cJ63667B66 1 V cJ63667B66 1 V cJ63667B66 1 V cJ63667B66 1 V cJ63667B66 1 V
Table 2. RSCM R² values of matrix and inclusion CM throughout the studied reaction zone.

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<th>Zone 3</th>
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6i ε 4usCN63E a a@dsu J6 1 V v csaus3ds=ëYH YR4=sd7Yë 63Gdsdq 4Gj
ës a@dsu J6as3ds ëYH d5 3Gg@dsu H Jd 3GY 7usd6ë ε6 i εls
usCN63E a a@dsu J6 1 V v Rhuscnsaus3ds=ëYH R4s a@dsu csaus3ds
eYH 36c FYë ës a@dsu 36c 36sq a@dsu3ë J6aus3 ds=ëYH s3a4 ε6 i
eës usCN63E a a@dsu J6 1 V v cuY7dëYH YR4s d7Yë63Gdsd ës a@dsu
the observed decrease in CM across the investigated lithological boundary is the result of a fluid-mediated process that happened at HP conditions in the subduction zone. Primary variations in the bulk CM content inherited from the protolith rocks may also be present locally but cannot explain the systematic patterns documented along several tens of lithological boundaries of various nature (Figs. 1-5). The detailed characterization of one reaction zone presented in Figures 5-8 clearly indicates that CM was initially present throughout the reaction zone and progressively removed towards the contact with the adjacent metagabbro (see Section 4.1). The preservation of characteristic microstructures of the protolith CM-bearing pelitic schist within the fluid-deposited lawsonite blasts (Fig. 4) also indicates that the CM inclusions in lawsonite represent relics of the CM initially present in the rock. The Raman analysis additionally confirms that the relict CM preserved as inclusion in lawsonite/titanite across the reaction zone is analogous to the CM of the starting metapelitic rock (Fig. 8). This feature rules out the possibility that the CM inclusions precipitated from the fluid together with the host lawsonite. The observed microstructural patterns of CM depletion in Z3, e.g. CM-rich lawsonite cores and CM-free lawsonite rims, also suggest that the CM leaching happened during the same metasomatic event responsible for the precipitation of lawsonite at high-pressure/low-temperature conditions. The initial precipitation of lawsonite in the reaction zone (preserved in Z2-Z4) and associated H2O increase (Vitale Brovarone and Beyssac, 2014) indicate that the fluid responsible for the removal of CM was dominantly aqueous.

The geochemical patterns across the reaction zone provide insights into the driving mechanism for CM leaching. Two alternative hypotheses are discussed: a redox gradient between the two adjacent lithologies in a static fluid, or the infiltration of an external fluid. In the first case, the dominant mechanism of mass transport is diffusion, and a chemical gradient between the metagabbro and the metapelite is expected. Conversely, a more complex pattern potentially including selective mass loss/gain in both lithologies may result from fluid-rock interaction mediated by advection of an external fluid. In the selected metasomatic halo (Fig. 5), a chemical gradient controlled by diffusion in a “closed” metasediment-metagabbro system would require some kind of C reprecipitation at the contact between the two lithologies or in the metagabbro, which is not observed (Fig. 6). The general behavior of fluid-mobile elements such as K, Rb, Ba and Cs across the reaction zone is characterized by a marked mass loss on both sides of the contact. Na may suggest a diffusive exchange between the metagabbro and the metapelite (Fig. 9). Nevertheless, the behavior of Na, as well as Ca and Sr, may reflect different fluid-rock equilibration between the fluid and either the metapelite or the metagabbro, perhaps involving some component of mechanical dispersion. Moreover, coupling the Ca and Sr profiles with the observed mineralogical evolution across the contact suggests a protracted fluid-rock reequilibration with initial precipitation (preserved in Z2-Z3) and successive destabilization
(Z4-Z5) of lawsonite (see Section 4.1 for details). As a whole, the above evidence suggests a dominantly advective mechanism of mass transport from an external fluid source.

The field data also suggest that the externally-derived fluid was primarily channelized parallel to the regional schistosity. Individual samples at the transition from Z2 to Z3 show discrete, foliation-parallel zones of bleaching. Moreover, the individual CM-leached, lawsonite-bearing veins identified within the metasedimentary pile are also parallel to the regional schistosity (Fig. 2c). This feature is in agreement with several previous studies indicating that fluid flow is greatest parallel to lithological boundaries or foliations (Ague, 2014 and references therein).

During progressive loss of CM from the rock, the fluid must have been at least transiently enriched in C. Increases in fluid C concentration may have affected the stability of mineral assemblages within the reaction zone. For example, increasing C content in the fluid may favor the breakdown of lawsonite (Nitsch, 1972), which occurred at least transiently in Z4 (Section 4.1). The formation of CO₂ may also lower the solubility of SiO₂ in metamorphic fluids (Newton and Manning, 2009), which could explain the increase of quartz modal amount in Z4.

Nevertheless, recent experimental studies suggest that CO₂ in graphite-saturated COH systems may strongly increase in the presence of aqueous SiO₂ and the formation of organic complexes (Tiraboschi, 2018; Tumiati et al., 2017). Following these results, the extensive quartz precipitation in Z4 may be ascribed to a process of C dilution in the fluid by either infiltration of aqueous fluids, or the in-situ breakdown of metasomatic lawsonite.

5.2. Selective dissolution of subducted disordered CM

Our data indicate that the more disordered CM component of the studied samples was more affected by the fluid infiltration than the crystalline CM. This phenomenon requires consideration of the origin of the two CM types and the related implications for bulk CM dissolution. Based on observations from both present-day sedimentary basins and metamorphic complexes, the CM present in metasedimentary rocks may have three different origins. The first and most common type is the metamorphosed biomass of the protolith sedimentary rock.

The second type is the so-called detrital CM, which derives from the erosion of exposed CM-bearing rocks, burned organic material, or any other source of CM-bearing materials. Studies conducted in active sedimentary environments indicate that detrital CM preserved in sediments is typically rather crystalline (low R² values) (Bouchez et al., 2010; Galy et al., 2008). The third type is graphitic C deposited by C-saturated fluid (Cesare, 1995; Galvez et al., 2013).

The Raman analysis across the selected reaction zone indicates the presence of two CM populations being characterized by either disordered CM (high R²) and nearly crystalline graphite (low R²) (Fig. 8). The presence of these two populations throughout the reaction zone, including in the metapelite unaffected by fluid-mediated transformations, indicates they were...
<table>
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<th>Loss OC per 100g rock</th>
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Page dimensions: 595.0x842.0
to Z1). The resulting CM mass loss for 100 g of rock relative to Z1 is 0.03 g (± 0.05) in Z2, 0.12 g (± 0.01) in Z3, and >0.12 g and >0.13g in Z4 and Z5, respectively (CM content in Z4–Z5 is below detection limits). The higher uncertainty in the weakly altered Z2 is most probably explained by primary heterogeneities larger than the mass change, and/or the amount of mass change was heterogeneously distributed within Z2. At least the latter hypothesis was observed within a single thin section of Z2, with CM leaching being more pronounced along discrete foliation-parallel layers (Fig. 5). For comparison, fractional CM loss across the reaction zone was also calculated considering Hf and Th as the least-mobile elements and yielded very similar results to Zr (Table 3). The calculations are actually fairly insensitive to the reference element chosen for Z3–Z5 because the percentages losses of CM are so large.

5.3. Fluid-rock regime of CM dissolution

As previously observed in sedimentary environments (Bouchez et al., 2010; Galy et al., 2008) and predicted for metamorphism (Connolly, 1995; Ziegenbein and Johannes, 1980), the response of CM to fluid-rock interactions may be different depending upon its degree of graphitization (Souche et al., 2012). From a thermodynamic point of view, disordered CM is a metastable phase during metamorphism, and a fluid in metastable equilibrium with such material is theoretically enriched in C compared to pure/crystalline graphite(Ziegenbein and Johannes, 1980) (Tumiati et al., 2020). Flushing of this material by aqueous fluids and protracted fluid-rock equilibration is therefore expected to selectively remove disordered CM from the rock with respect to a more crystalline CM, and our Raman spectroscopy dataset confirms this theoretical assumption. Nevertheless, the widespread preservation of disordered CM in the regional metapelitic rocks unaffected by strong fluid-rock interaction indicates that this expectation becomes relevant only in the case of major fluid infiltration; the approximation of CM to pure graphite for thermodynamic calculations appears to be reasonable in closed systems.

Equilibria between fluids and CM have been classically described in the COH system (Connolly, 1995; Holloway, 1984). In this system, any fluid in equilibrium with CM is expected to lie on a metastable CM-saturation curve. The position of the curve is dependent on the P and T conditions, and on the crystallinity of the CM (Ziegenbein and Johannes, 1980). The concentration of C in a graphite-saturated COH fluid in equilibrium with CM increases with increasing T, with decreasing P, and/or with decreasing crystallinity of the CM. An increase in CM crystallinity, in the case of subduction metamorphism, would also require an increase in T.

Therefore, the observed CM leaching could be explained by an infiltrating fluid migrating along either an up-T or a down-P gradient. Up-T fluid circulation has been proposed in the metamorphic units of Alpine Corsica, but within inherited fractures unrelated to the regional
In the present case, field relationships suggest that the fluid flow was dominantly foliation-parallel, which in a simple slab thermomechanical configuration would correspond to a slab-parallel, down-T flow. However, because a down-T, down-P flow would lead to C precipitation rather than leaching (Cesare, 1995), an up-dip fluid flow along a rather constant T (i.e., along a slab parallel geotherm) is the most likely condition to dissolve C at the considered conditions.

Alternatively, or complementary to an isothermal up-dip gradient, another mechanism can be proposed based on the recent experimental and thermodynamic results by Tumiati et al. (2017). The authors showed that the C concentration in a graphite or, more generally, CM-bearing system can vary by 30% in the presence of dissolved SiO$_2$ relative to a pure COH system, and without significant variations in fO$_2$. This was explained by the formation of organosilicon complexes in the fluid (Tumiati et al., 2017). The complex evolution of the studied metasomatic aureole preserved from Z2 to Z5 clearly documents fluid-rock variations involving initial lawsonite precipitation (preserved in Z2) and successive consumption (Z3-Z5). The precipitation of abundant quartz in Z3-Z5 demonstrates aqueous SiO$_2$ oversaturated conditions that could have favored the extreme CM depletion in the same zones. We therefore propose that the mechanism of fluid-mediated CM removal was driven by either a down-P gradient, or by modifications of the dissolved SiO$_2$ in the fluid-rock system, or a combination of them.

### 5.4. Fluid fluxes responsible for selective CM dissolution

The removal of disordered CM relative to the more crystalline CM allows assessment of the aqueous fluid fluxes required to achieve the observed CM removal in the field area. Flux estimates were calculated based on the predicted C solubility in fluids in equilibrium with either crystalline graphite (lower solubility) and glass-like C (higher solubility) (Tumiati et al., 2020; see section 3.4 for details). Glass-like C is not expected to be present in natural samples of metamorphic rocks but is considered here as a low solubility reference compared to graphite based on the available thermodynamic data at the considered P-T conditions (Tumiati et al. 2020). Under the assumption that the studied CM was chemically pure (see Section 3.4), the observed selective removal of disordered CM indicates that this phase was metastable relative to graphite. This would imply that the disordered CM was more soluble than graphite. However, because thermodynamic data for the disordered CM present in the natural samples are not available, the higher or lower solubility of this material relative to the glass-like C used by Tumiati et al. (2020) cannot be assessed. The range of CM solubility considered in this study therefore provides a qualitative constrain on the magnitude of aqueous fluid infiltration responsible for the selective removal of disordered CM relative to more crystalline CM.
R3FG d Yad é 4ls a3GgGéSc aq5 ggéhs hYgS sd YTh T usvglsuc éY5 YFqís s sjé4su Cu74Jóls YucGddl As 1 3aaYw6C éY éls a3GGGéSc RbaéY6xG5 3dd Ýddsd 7usv 5 YPU4a BsaéY6 R4s u5dGd6€C q ß4ruY3a3 3G0Y dYq6 R3FG AYu3 Chs6 T FgBiu dga4 3d éls b T 5 3xj5 g5 étsdb u6YdYdl a Y6éh3éhls 3d Y6G4él RbaéY6YFqís usvglsuc éY5 YFqís éls 1V q 3d aY6é>dusuc d q 3sùùa ú éYYd7uYhYs Y6G3uBGóJ6Ypó3 3éY6 Y6 éls 5 sa43Jéls d YP RáJq uY a J6éubéY6 éls éls s J6éCúéSc RáJq RáJqsd Cgs 3g5Cáésu 36c Asú( usvglsuc éY3aJ4shs éls YFadusuc 1V Ýddsd q sjé s dsé 3eC 3auYd54s8sáY6) Y6s3dC dggdscj 6BsaéY6 RJ5 s J6éCúéSc RáJq RáJqsd L3us a3GgGéSc q J6 s vsg3GJY6 J6 Cgs é4éJdH3Cé PHYU chsaéY6cY5 J6ésscd (dés5 dq Jé4 d5 G0YyDk( φ

, 4sus Jd é4s cldé6as YPó4s CsYa6s5 Ja3CRIy6€7uY7C3B6Y6 Jd é4s 6g5 Fsu YP5 Y6d YP aY6g5 sc 7sug6jéhYG6 s 5 YGY sdé5 3èc RY5 5 3dd F3G6as 363GdJd ≃Jd é4s RáJq aY57YdýY643éq YgG F6s J6 s vsgJOFalq5 q Jé4 é4s 5 J6suBGSd5s FGc 36c q ≃Jd é4s
initial fluid composition. $C_{i}^{eq}$ corresponds to the experimentally determined solubility of either

glass-like C or graphite (Tumiati et al, 2020), whereas $C_{i,x=0}^{inpt}$ is set to zero in order to have the

most conservative results. Results are presented in Table 5.

The results, shown in Figure 10, are dependent on the distance of reaction front propagation

(L), which corresponds to the distance of fluid percolation parallel to the lithological boundary.

The parameter $n$ on the vertical axis is the log$_{10}$ of L expressed in meters. For example, for L = 10 m, $n = 1$.

Three general patterns are observed: (i) the time-integrated fluid fluxes ($q_{TI}$) required to achieve

the observed CM losses decrease with increasing T and P, in agreement with the general

behavior of the COH system at C-saturated conditions (Connolly, 1995; Holloway, 1984); (ii) at a given P-T condition, the flux is higher for graphite relative to glass-like C, in agreement

with earlier studies (Ziegenbein and Johannes, 1980); and (iii) the $\Delta q_{TI}$ between graphite and

glass-like C ($\Delta q_{TI, graphite-glass-like C}$) decreases with increasing P (and T to a lesser degree, Tumiati

et al., 2020). More specifically, the $\Delta q_{TI, graphite-glass-like C}$ is of the order of $1.8 \cdot 10^{n}$ m$^{3}$/m$^{2}$ at 300

°C and 1 GPa, $0.8 \cdot 10^{n}$ m$^{3}$/m$^{2}$ at 370 °C and 1.3 GPa, and $0.5 \cdot 10^{n}$ m$^{3}$/m$^{2}$ at 425 °C and 1.7

GPa.

The profiles in Figure 10 also indicate that the fluid flux was higher close to the lithological

boundary and progressively decreased towards the metasedimentary rocks in a way consistent

with the numerical simulations of Ague (2007) for fluid flow in mélange systems. Variations

in the size and geometry of the reaction zone and magnitude of fluid flux are expected

depending on the size and shape of the blocks (Ague, 2007).

The above calculations show that degree of CM crystallinity has a lower effect on the selective

dissolution of disordered CM at P-T conditions of 1.7 GPa and 425°C (peak conditions for the

selected aureole) relative to lower-grade conditions (Fig. 10). The field isograd for the

companion lawsonite metasomatism and CM leaching suggests that this fluid-mediated process

took place at conditions of $\sim 370$ °C and $\sim 1.3$ GPa in Alpine Corsica. At these conditions, the

$\Delta q_{TI, graphite-glass-like C}$ is slightly higher compared to peak conditions (Fig. 10). We therefore

suggest that the selective leaching was achieved during the prograde path of the selected rocks

where the difference in solubility between disordered CM and graphite was higher. In the

Western Alps, evidence for CM leaching in equivalent lithological contexts was observed at

lower T in the range of 340 °C (Fig. 1), suggesting slightly different regional fluid flow patterns,

but likely similar orders of magnitude compared to Corsica, as discussed in the next section.
null
relative to the estimated fluxes would result in removal of crystalline graphite. It is not
excluded, at least in Z5, that some of the more graphitic CM was actually removed from the
rock. In any case, the fluid-mediated dissolution of CM documented in this study, as well as
the experimental data by Tumiati et al. (2020), indicates that a region of potential release of
significant amounts of C through fluid-mediated mobilization of disordered CM may exist in
subduction zones. Prograde infiltration of aqueous fluids through rocks containing disordered
CM may therefore exert a negative feedback on the sink of refractory C-bearing phases into the
mantle by subtracting a fraction of the subducted organic C from the rock prior to full
graphitization. Fluid channelized along the top of the subducting slab, or along the base of the
slab sedimentary rocks, has potential to mobilize significant amounts of reduced C, and thereby
impair a light $\delta^{13}$C signature to the slab-derived fluids transferred to shallower reservoirs.
Considering the $\delta^{13}$C signature of CM at the relevant metamorphic conditions in carbonate free
metasediments of $\sim$-25‰ (Cook-Kollars et al., 2014), and the fluid speciation of graphite-
saturated systems at the H$_2$O-maximum, the fluid generated by the CM dissolution would have
$\delta^{13}$C of $\sim$-25‰ and -23‰ at 300 °C and 425 °C, respectively (graphite-CO$_2$ and graphite-CH$_4$
fractionation factors from Bottinga et al 1969). A possible natural example of generation and
circulation of such fluids are documented by Spandler et al. (2008), who reported isotopically
light, fluid-deposited carbonate (as low as -12‰) in metasomatized sequences from the
metamorphic belt of New Caledonia. In the same terrane, metasedimentary rocks are CM-
depleted compared to equivalent sequences unaffected by intense fluid circulation (Vitale
Brovarone et al., 2018a).

6. CONCLUSIONS

We collected field, microstructural, geochemical, and thermodynamic data showing that
channelized, fluid-mediated dissolution of CM can be an efficient process at forearc depth in
subducting slabs. Our study shows that, within individual samples, the removal of CM was
more efficient for disordered CM relative to crystalline CM, providing a means to constrain the
magnitude of fluid fluxes at different depths within the subducting slab. The data collected
herein indicate that the order of magnitude of fluid fluxes along channelized pathways at
blueschist-to-eclogite-facies conditions is large enough to potentially remove the entire amount
of organic C from a given volume of rock, but only in the presence of channelized fluid flow.
The widespread distribution of fluid-mediated removal of CM along lithological boundaries in
two investigated mountain belts indicates that the estimated magnitude of channelized fluid-
fluxes can be common in the forearc regions of subduction zones where subducted CM is
structurally disordered. This fluid-mediated process is expected to mobilize significant amounts
of isotopically light, reduced C along the top of the slab or at the base of the subducted sedimentary crust.

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