Abiotic formation of condensed carbonaceous matter in the hydrating oceanic crust

Marie Catherine Sforna1,5, Daniele Brunelli1,2, Céline Pisapia3,4, Valerio Pasini1,3, Daniele Malferrari1 & Bénédicte Ménez3

Thermodynamic modeling has recently suggested that condensed carbonaceous matter should be the dominant product of abiotic organic synthesis during serpentinization, although it has not yet been described in natural serpentinites. Here we report evidence for three distinct types of abiotic condensed carbonaceous matter in paragenetic equilibrium with low-temperature mineralogical assemblages hosted by magma-impregnated, mantle-derived, serpentinites of the Ligurian Tethyan ophiolite. The first type coats hydroandraditic garnets in bastitized pyroxenes and bears mainly aliphatic chains. The second type forms small aggregates (~2 µm) associated with the alteration rims of spinel and plagioclase. The third type appears as large aggregates (~100–200 µm), bearing aromatic carbon and short aliphatic chains associated with saponite and hematite assemblage after plagioclase. These assemblages result from successive alteration at decreasing temperature and increasing oxygen fugacity. They affect a hybrid mafic-ultramafic paragenesis commonly occurring in the lower oceanic crust, pointing to ubiquity of the highlighted process during serpentinization.
At slow and ultraslow Mid-Ocean Ridges (MORs), mantle-derived rocks are progressively serpentinized by aqueous fluids that circulate through the upper lithosphere. By producing H₂-bearing fluids, these environments are considered to be favorable for the chemical reduction of magmatic inorganic carbon species (CO/CO₂) or seawater carbonate ions ¹–². Up to now, abiogenic methane (CH₄), short-chain hydrocarbons and carbonyl acids were accordingly identified in hydrothermal fluids discharged at MORs³–⁷ or in products from analog experiments⁸–⁹. However, experimental studies and thermodynamic calculations have recently shown that carbonaceous phases should be dominantly produced during serpentinization¹⁰,¹¹. Yet natural occurrences of Condensed Carbonaceous Matter (CCM) were rarely reported. Graphitic CCM aggregates, sometimes considered as biologic in origin, have been identified in serpentinites from the Mid-Atlantic Ridge⁴–¹⁶ and in serpentinized gabbroic and peridotitic xenoliths ¹⁷–¹⁹.

The samples here described were collected in the Northern Apennine ophiolites, which are lithospheric remnants of the Piedmont-Ligurian oceanic basin, a branch of the Mesozoic Tethys ²⁰ (Fig. 1). The oceanic sequence is formed by mantle peridotites, once exposed at the seafloor, intruded by sparse gabbroic bodies and a discontinuous basaltic cover. This association presents strong similarities with present-day non-volcanic passive margins and ultra-slow spreading ridge settings ²⁰,²¹. Our study focuses on a small serpentinitic body (150 m-long; Fig. 1b) pertaining to the Val Baganza unit of the External Ligurides ²².

Fig. 1 Sampling location and geological maps. a General map of the ophiolite outcrops in Emilia-Romagna (Italy) and sampling location (red star) modified from ref. ⁵⁴. b Geological map of the sampling location, modified from ref. ⁵⁵.

Results
A multistage aqueous alteration history. The protolith of the studied serpentinite is a mantle-harzburgite, equilibrated in the spinel-stability field, impregnated at high temperature (~1200 °C) by a percolating melt as attested by the presence of secondary magmatic spinel and plagioclase ghosts (Supplementary Fig. 1). The progressive retrograde hydration trend of the protolith is recorded by a sequence of temperature-decreasing parageneses. The pervasive high-temperature serpentinization assemblage (T>300 °C) ²⁴ is characterized by mesh textured lizardite + magnetite and bastite (i.e., fine-grained lizardite), substituting primary olivine and orthopyroxene, respectively (Supplementary Fig. 1, Supplementary Tables 1, 2). These textural and mineralogical relationships closely match those formed during present-day serpentinization of abyssal mantle peridotites ²⁴, ²⁵.

The serpentine groundmass presents discrete microtextual domains hosting different parageneses. Residual and magmatic spinels developed inward ferrichromite (Ft) rims (Supplementary Fig. 1, Supplementary Tables 3, 4). The ferrichromite is itself composed of a submicrometric association of Cr-magnetite (Cr-Mag), chlorite and lizardite; it displays low Fe³⁺# (100 × Fe³⁺/(Fe³⁺ + Cr + Al); mean = 25.87 ± 12.76; Supplementary Table 4), suggesting low temperatures of alteration (≤200 °C) ²⁵. Ferrichromite is commonly surrounded by outward chlorite rims (Chl1), resulting from the interaction between the surrounding serpentine and the cations (Mg²⁺, Al³⁺) released during the spinel alteration ²⁶ (Fig. 2, Supplementary Fig. 1, and Supplementary Tables 5, 6).

After the development of the ferrichromite rims we observe four low-temperature micro-parageneses. The first, named BastHadr, is composed of elongated and chemically-zoned hydroandraditic garnets (Hadr-1; Fig. 3) hosted in bastitic serpentinite replacing orthopyroxene. The hydroandradites are rich in Ti and Cr (Supplementary Table 7) and grew following the clinopyroxene exsolution lamellae within orthopyroxene. They display narrow and elongated cavities filled with lizardite (Fig. 3c). The second paragenesis is composed of cryptocrystalline clinoclore ± lizardite ± hydroandradite pseudomorphs on plagioclase (Chl ± Srp ± Hadr-2; Fig. 2, Supplementary Tables 8, 9). Unlike Hadr-1, these hydroandradites (Hadr-2) are made of nanocrystalline selvages, poor in Cr and Ti (Supplementary Table 9). The third assemblage, made of Fe-rich Mg-saponite and hematite (HemSap; Fig. 2) is located only within the plagioclase ghosts, suggesting that it derives directly from plagioclase relics or from the Chl2 ± Srp ± Hadr-2 assemblage. Although a replacement of plagioclase relics cannot be completely excluded, the HemSap domains and the Chl2 ± Srp ± Hadr-2 domains clearly intertwine (Fig. 2b, c), with a decrease of the chlorite and hydroandradite proportions toward the domain borders, in favor of a progressive inward alteration of the Chl2 ± Srp ± Hadr-2 domain to saponite. Local interlayering of chlorite within saponite supports local replacement of Chl2 ± Srp ± Hadr-2 pseudomorphs after plagioclase (Supplementary Tables 10, 11). Saponite displays high content in Fe (up to ~7%Wt; Supplementary Table 10). In the same domains, hematite (Supplementary Table 12) forms rosettes interlocked with serpentine, saponite and chlorite. Hematite is always found in association with saponite but the reverse is not true, suggesting that hematite grew at the expense of saponite. Variably altered spinels are commonly preserved within the pseudomorphs (Fig. 2). The fourth low-temperature paragenesis...
contains large hydroandradites (Hadr-3; Fig. 2a and Supplementary Table 13) developed on the edges of serpentine veins (Supplementary Table 14), growing along serpentine fibers. Their Cr$_2$O$_3$ and TiO$_2$ contents are similar to Hadr-2 and Hadr-1, respectively (Supplementary Table 13).

**Multiple occurrences of condensed carbonaceous matter.** Significant amounts of CCM have been identified by scanning electron microscopy (SEM) and characterized by Raman and Fourier transform-infrared (FTIR) spectroscopies. CCM occurrences are associated with three out of the four low-temperature micro-parageneses described above, namely the bastite-hosted hydroandradite Hadr-1 (CCM-BastHadr), the pseudomorphed plagioclase (Chl2 ± Srp ± Hadr-2) coupled to the ferritchromite rims (CCM-PPFtc), and the hematite + Fe-rich Mg-saponite assemblage (CCM-HemSap) (Figs. 2–5). CCM aggregates display differences in size and composition among the various mineralogical assemblages. The rare and very small (~2 μm) CCM-PPFtc occurrences (Fig. 4) were not analyzed by Raman and FTIR spectroscopy due to intense fluorescence and their too small size, respectively.

The CCM-BastHadr appears as thin films (< 6 μm) coating Hadr-1 crystals and their inner cavities (Fig. 3). The associated Raman spectrum (Fig. 5, Supplementary Table 15) shows two large bands in the 1100-1450 cm$^{-1}$ region, corresponding to Cr$^{3+}$ luminescence in garnet [27]. Although these bands partially mask the organic signal, CH$_2$ and CH$_3$ vibration bands can still be recognized on their shoulders. Intense bands corresponding to aliphatic COOH (1532 cm$^{-1}$) [28] can be observed in the 1400-1800 cm$^{-1}$ region. Another band corresponding to COO$^-$ stretching can be detected but no clear C=C vibrations characteristic of aromatic moieties were identified [29]. The CCM-HemSap assemblages form large aggregates up to 100–150 μm in size. They are mainly associated with hematite, filling the mineral embayments and cracks developed during the retrograde transformation of Chl2 ± Srp ± Hadr-2 into Fe-rich Mg-saponite (Fig. 2). The associated Raman spectrum displays CH$_3$ and CH$_2$ vibrations suggesting the presence of aliphatic chains, as confirmed by FTIR spectroscopy (Supplementary Fig. 2). The mean methylene to methyl ratio R$_{CH2}$:CH$_3$ (1.47 ± 0.45; Supplementary Table 16) indicates short aliphatic chains, bearing up to 6–8 carbon atoms [30]. Contrarily to CCM-BastHadr, CCM-HemSap assemblages display several vibration bands characteristic of aromatic moieties (Fig. 5, Supplementary Table 15).

**Discussion**

The strict spatial association between the organic and mineralogical phases suggests that the different forms of CCM are in paragenetic equilibrium with secondary mineral phases. This observation, supported by the systematic association of a given CCM type with a given mineral paragenesis, indicates that CCM formation could have occurred simultaneously to the growth of the host mineralogical assemblage, thus suggesting an abiotic endogenic genesis. Additionally, the CCM spectral signatures reported here (Fig. 5) lack evidence of protein-forming amide groups of biological origin, such as those previously reported in oceanic serpentinites [14,15]. A CCM genesis after thermal degradation of pristine biogenic material can also be excluded based on Raman spectra that do not display the expected broad bands of...
graphitic carbon (~1340–1360 and 1580–1610 cm$^{-1}$) that would be produced by this process.

Casale samples show that the amount of CCM varies among the observed mineral assemblages: minor in the plagioclase pseudomorphs coupled to the ferritchromite rims (CCM-PPFtc), more important in the BastHadr domains (CCM-BastHadr) and massive in the HemSap paragenesis (CCM-HemSap). The last two CCM pools while presenting a similar aliphatic character, differ in their carboxylic pattern: the CCM-BastHadr assemblage shows a higher content in carboxylic functional groups whereas aromatic carbon is present in the CCM-HemSap assemblage. While the hydration of olivine was considered as the only putative reaction pathway for CCM formation in recent thermodynamic calculations, these observations are suggestive of differential formation pathways and productivity possibly implying differences in the synthesis mechanism and limiting factors at local scale.

The formation of non-graphitic CCM in serpentinization-related systems was thermodynamically predicted to occur during olivine serpentinization in the 200–400 °C temperature interval. At these temperatures CCM forms preferentially provided that CH$_4$ is kinetically inhibited. Our data confirm and significantly extend CCM abiotic synthesis to diverse mafic and ultramafic mineral precursors and lower temperature ranges. Overall, the low-temperature parageneses found in the Casale serpentinite are progressive steps of a low-temperature alteration sequence resulting from increasing oxidizing conditions occurring during the uplifting of the oceanic mantle and its exposition to the seafloor. The crystallization and stability fields of these low-temperature assemblages give constraints on the formation of CCM-BastHadr and CCM-PPFtc assemblages during hydrothermal alteration at depth in an oceanic subaxial environment (< 10 km). The crystallization of hydroandradite occurs at temperatures < 200 °C, low oxygen fugacity, low CO$_2$ partial pressure and low silica activity. The CCM-HemSap assemblage was formed later at lower temperatures, higher silica activity and in a
Dihydrogen availability released by mineral reactions is likely not the only factor impacting local CCM productivity. Below 200 °C, the presence of a catalyst is required to initiate carbon reduction reactions\(^5\). For instance, provided that the fluid contained comparable inorganic carbon content, CCM is not systematically found in association with hydroandradite even though its formation produces 1 mole of H\(_2\) per mole of hydroandradite crystallized\(^5\). Significantly, CCM appears associated with the hydrogarnets of the BastHadr associations (Hadr-1) that show Cr-rich rims containing up to 2.7%Wt of Cr\(_2\)O\(_3\) (Supplementary Table 7). Cr\(^{3+}\) is an efficient catalyst\(^3\) and may have played a catalytic role at the surface of Hadr-1, promoting the peripheral formation of the CCM-BastHadr assemblage. Conversely, the CCM-PPFtc occurrences are limited to thin films on the spinel borders and thin nuggets dispersed in the surrounding Chl2 ± Srp ± Hadr-2 pseudomorphs on plagioclase (Fig. 4). Hadr-2 has in fact low amount of Cr\(^{3+}\) (mean Cr\(_2\)O\(_3\)=0.4% Wt; Supplementary Table 9), thus a likely low catalytic capability. Moreover, while spinels are thought to promote organic synthesis\(^3,51,52\), the growth of Fe\(^{3+}\)-hydroxides at their surface during alteration can limit internal Fe\(^{2+}\)-oxidation and associated H\(_2\) delivery\(^48\). This is supported by the low measured Fe\(^{3+}\)/# of the spinel Ftc rims ( Supplementary Table 4). The surrounding para-genes is composed of Fe\(^{2+}\)-bearing phases (Chl1, Chl2, Srp, ferri-chromite i.e., Chl, Srp, Cr-Mag; Supplementary Tables 4, 5, 6, 8) suggesting an overall limited oxidation of the primary phase and hence limited H\(_2\) production. This mineral aggregation at the ferri-chromite surface may also have acted as barrier for Fe\(^{2+}\) diffusion from external sources that would have sustained a longer generation of H\(_2\) and thus higher CCM production.

The most abundant CCM accumulations are found in the HemSap domains. We propose they originate from the interplay between the capability of hematite to produce H\(_2\) during its formation\(^48,50\), and the cation exchange capacity of the saponite structure\(^5\), Octahedral Fe\(^{2+}\) and Fe\(^{3+}\) for Mg\(^{2+}\),\(^5\) and tetrahedral Al\(^{3+}\) and Fe\(^{3+}\) for Si\(^{4+}\) heterovalent substitutions in the Fe-rich Mg-saponite silicate layers (Supplementary Tables 10, 11) may create charge imbalances in the octahedral and tetrahedral sheets\(^5\). Moreover, saponite appears to be highly heterogeneous at the micrometric scale with varying quantities of Fe\(^{3+}\) and Fe\(^{2+}\) in various coordination numbers (Supplementary Tables 10, 11). The charge imbalance promotes the exchange of cations in the clay mineral interlayers\(^5\). It also provides catalytic acid sites in the tetrahedral layers that may promote direct adsorption/intercalation, retention, and polymerization of organic compounds\(^5\). Chemical formulas calculated for the Fe-rich Mg-saponite also reveal a high octahedral occupancy that nicely agrees with the possible presence of transition metals (Cr, Ni, Fe, Mn, and Mg; Supplementary Tables 10, 11) in the saponite interlayers. These cations could further promote the complexation of organic compounds\(^5\). Coupled to the H\(_2\) produced during the crystalization of hematite, this would promote further CCM formation.

Microscopy and microspectroscopy techniques allowed for the first time to document the occurrence of different types of abiotic condensed carbonate matter within natural serpentinites. These occurrences are strictly associated with particular low-temperature mineralogical assemblages, suggesting that the organic material is in paragenetic equilibrium with each mineral assemblage. As compiled in Fig. 6, the formation of the different assemblages occurs at decreasing temperatures and (slightly) increasing dissolved O\(_2\) concentrations, showing that CCM formation does not occur in a single event during aqueous alteration of the oceanic lithosphere. The slight change in oxygen concentrations necessary to produce Fe\(^{3+}-\)oxides\(^5\) is likely not sufficient to prevent the continuous formation of CCM given that the saponite and hematite surfaces provide locally reducing micro-domains\(^48\). The combination of enhanced H\(_2\) production due to hematite crystallization coupled to
the saponite/hematite catalytic capabilities is a possible highly efficient engine to produce large CCM accumulations. Such process could be widespread in mafic/ultramafic-hosted hydrothermal systems at MORs, thus storing effectively organic carbon below the oceanic seafloor in a relatively immobile form. The condensed carbonaceous material can be preserved on the long term like in the Casale samples here described, or serve as carbon sources for deep microbial ecosystems, with also the potential to impact abiotic synthesis pathways including dihydrogen or methane generation.

Methods

Sample preparation. To limit any laboratory contamination, samples were carefully prepared in a clean organic-free environment. Inner cores of the collected samples were extracted with a saw treated with 5% sodium hypochlorite. Cutting
Fourier transform-infrared microspectroscopy. FTIR measurements were performed on a Thermo Scientific Nicolet iN10 MX imaging microscope (IPGP, Paris, France). Data were acquired with a conventional Ever-Glo™ infrared source equipped with a x 15 objective (NA = 0.7) and a liquid nitrogen cooled MCT-A detector. Spectra were collected as punctual analysis or in mapping mode. In punctual analysis mode, spectra were recorded in a 20 μm² sample area, the spectral acquisition range was 600–4000 cm⁻¹, well below the critical dose of radiation that can damage carbonaceous material. This configuration yielded a planar resolution close to 1 μm. Acquisitions were obtained with an 1800/5 mm grating illuminating a Pelletier-cooled 1024 × 256 pixel CCD array detector. Punctual analyses were carried out in static mode with a spectral detection range of 200–2000 cm⁻¹. Beam centering and Raman spectra calibration were performed daily on a quartz crystal with a characteristic SiO₂ Raman band at 463.5 cm⁻¹. To exclude any organic contamination, carbonaceous matter spectra collected on conventional thin sections were systematically compared to the ones obtained on resin- and glue-free samples. Data were processed with LabRAM™ and WIRE 3.3™ softwares.

Electron microprobe analysis. Mineral chemistry was characterized by electron microprobe analysis (EMPA) with the Cameca SXFive installed at CAMPARIS, University Pierre et Marie Curie (Paris, France). Thin sections were coated with carbon once all the other analyses were achieved. Operating conditions were 15 kV and ~10 nA. Analyses were acquired in punctual mode and in stage map mode (grid pattern). Maps (300 × 250 pixels) were generated with a 1 μm step and a 0.1 s dwell time. For each pixel characteristic of a mineral, the percentage in weight (%) of each element analyzed and mineral formula were retrieved (Supplementary Tables 1-5, 7-10, 12-14).

Data availability
The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information File.

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Author contributions

M.C.S., D.B., C.P., V.P., D.M., B.M. acquired and treated the data. M.C.S, D.B. and B.M. wrote the paper with input from all the co-authors.

Additional information

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