Subduction hides high-pressure sources of energy that may feed the deep subsurface biosphere

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Geological sources of H₂ and abiotic CH₄ have had a critical role in the evolution of our planet and the development of life and sustainability of the deep subsurface biosphere. Yet the origins of these sources are largely unconstrained. Hydration of mantle rocks, or serpentinization, is widely recognized to produce H₂ and favour the abiotic genesis of CH₄ in shallow settings. However, deeper sources of H₂ and abiotic CH₄ are missing from current models, which mainly invoke more oxidized fluids at convergent margins. Here we combine data from exhumed subduction zone high-pressure rocks and thermodynamic modelling to show that deep serpentinization (40–80 km) generates significant amounts of H₂ and abiotic CH₄, as well as H₂S and NH₃. Our results suggest that subduction, worldwide, hosts large sources of deep H₂ and abiotic CH₄, potentially providing energy to the overlying subsurface biosphere in the forearc regions of convergent margins.
Deeply sourced H2 and CH4 in fluids are potentially important contributors of energy and carbon supporting the habitability of the largest microbial habitat on Earth, the deep subsurface biosphere. The identification of geological processes releasing these compounds is vital in understanding natural energy, carbon cycling, and the extent and magnitude of deep life. Additionally, the identification of abiotic sources of energy such as H2 and hydrocarbons provides key information about the parameter space for the emergence of life on Earth, and on where life could exist elsewhere. Aqueous alteration of mantle rocks, or serpentization, is considered a key process releasing H2 and promoting the abiotic synthesis of CH4. Production of H2-Ch4 fluids through serpentization has been identified at mid-ocean ridges, on-land, and in the shallow forearc of subduction zones. Strong evidence exists that deep microbial communities take advantage of serpentinite-sourced H2-Ch4, and the identification of key building blocks of life in serpentinized ultramafic rocks supports the hypothesis that these settings could have witnessed the emergence of life on Earth.

Geochemical data from forearc mud volcanoes and hydrothermal seeps suggest that life exists as deep as 15 km below the surface at convergent margins, and that the essential carbon to sustain deep microbiological habitats in the forearc of convergent plate margins is provided by the metamorphic recycling of subducting slabs. However, the composition and redox state of fluids released from subducting slabs, and therefore their capability to sustain different forms of a deep biosphere in the forearc is unconstrained. Most models consider slab-derived fluids to be rather oxidized and dominated by CO2 (refs. 19, 20). However, thanks to the anomalous geothermal regimes of subduction zones which stabilize serpentine minerals to depths of ~100 km, serpentinization of deep-seated mantle rocks may represent a suitable environment for the genesis and migration of deep H2 and abiotic CH4. The delivery of these gases to the subsurface biosphere from the deep Earth could dramatically change our understanding of deep carbon cycling at convergent margins and the distribution and magnitude of deep life on Earth.

Serpentinization of mantle sections at convergent margins has been identified by geophysical investigations and numerical simulations. Furthermore, H2 and CH4-rich fluids have been detected in subduction-zone metamorphic rocks. However, it has been proposed that serpentinitization of deep-seated mantle rocks at high temperature in subduction zones may not involve Fe oxidation and formation of Fe3+-bearing minerals such as magnetite, thereby inhibiting the release of H2 and genesis of abiotic CH4. Whether serpentization to produce H2-Ch4-rich fluids occurs at high pressure (P) and temperature (T) conditions remains an open question.

Here, we investigate the patterns of serpentization of ultramafic rocks within the stability field of antigorite, the high-temperature serpentine polycrystal characteristic of high-pressure metamorphic conditions at depths >40 km in subduction zones. We present results from three different sections of Alpine paleo-subduction complexes. We show that intense high-pressure serpentization happened in the subducting slab and was accompanied by reducing conditions and release of H2-Ch4-rich fluids at depths of about 40–80 km. As serpentization also affects the mantle wedge above subducting slabs, our results suggest that subduction zones may represent large source regions of H2 and abiotic CH4 on Earth, with important consequences for the mobility of deep C and the genesis of high-pressure sources of energy. In addition to H2 and CH4, our data show that other strongly reduced compounds such as H2S and NH3 can form in deep serpentization fluids, a result that has implications for the diversity and distribution of deep subsurface communities at convergent margins.

Results

Relative timing of serpentinitization. Constraining the timing of serpentization in metamorphic serpentinites from mountain belts is challenging owing to the similarities between serpentinites resulting from multiple events (e.g., ocean floor; subduction; exhumation) or from single hydration events. The presence or absence of specific serpentine polydose can provide constraints on the temperature range of serpentization. For example, lizardite is generally stable at low temperatures and antigorite at high temperatures. However, this is useful only under the assumption of single hydration events, which can hardly be expected in a large fraction of exhumed metamorphic serpentinites. Furthermore, the mineralogy and microstructures of antigorite serpentinites formed from fresh peridotites at high-pressure conditions, and of subducted oceanic serpentinites recrystallized in the antigorite stability field could be very similar. And minerals formed during seafloor serpentization, such as magnetite, may be preserved as relict phases in metamorphosed serpentinites. Consequently, recognition of the potential of deep serpentization to generate H2-Ch4-rich fluids in subduction zones is difficult.

In order to overcome this difficulty, we investigated variably serpentinitized pseudotachylyte-bearing peridotites from the blueschist- to eclogite-facies terranes of Alpine Corsica and the Italian Western Alps. Previous studies have demonstrated that the formation of pseudotachylytes, i.e., seismically produced molten rocks, in these rocks happened at high-pressure conditions during the Alpine subduction zone. Because the formation of pseudotachylytes is inhibited in ultramafic rocks exceeding about 5 vol% serpentinitization, the antigorite serpentinitization of the selected ultramafic pseudotachylytes and their host rocks must have happened at high pressure in the subduction zone.

We studied serpentization of peridotite-hosted pseudotachylytes from the blueschist- to eclogite-facies Cima di Gratera, Alpine Corsica, and Monte San Petrone, Alpine Corsica (metamorphic climax 430 °C and 1–1.5 GPa), the eclogite-facies Lanzo massif, Italian Western Alps (2–2.5 GPa and 550–620 °C), and Monte San Petrone, Alpine Corsica (480–530 °C and 2.2–2.4 GPa). The ultramafic pseudotachylytes from the latter are reported herein for the first time (Supplementary Note 1, Supplementary Fig. 1). In these three case studies, pseudotachylyte-bearing fresh peridotite bodies are enclosed in strongly serpentinized rocks interpreted as metamorphosed oceanic serpentinites. The latter consist mainly of antigorite + magnetite ± brucite ± metamorphic olivine. Here we assume that their formation during the pre-subduction serpentization event (i) did not affect the studied fresh peridotite bodies, as indicated by the formation of pseudotachylytes, and (ii) was followed by a second stage of serpentization overprinting the pseudotachylyte-bearing peridotites at high-pressure conditions (Fig. 1).

Patterns and conditions of high-pressure serpentization. In the three selected case studies, the peridotite is composed of primary mantle olivine (Fo03), clinopyroxene, orthopyroxene and spinel, with local plagioclase veinlets, and is crosscut by deformation bands and pseudotachylytes ranging in thickness from less than 1 mm to several cm (Supplementary Note 2, Supplementary Fig. 2). The pseudotachylyte assemblage consists of the same mineralogy as the host rock, except for minor mineral compositional variations (Supplementary Table 1). The presence of spinel and absence of plagioclase in the pseudotachylytes in the three case studies constrain the formation of the pseudotachylytes...
to \( P > 1.1 \) GPa\(^{41}\), corresponding to depths greater than \( \sim 40 \) km. The rocks show various degrees of post-pseudotachylyte serpentinization, from incipient to rather complete (Fig. 1a–c). In order to minimize potential biases in our interpretations, we selected samples characterized by static serpentinization and no post-pseudotachylyte ductile deformation (Fig. 1a–c; Supplementary Figs. 3–5). The serpentinization proceeds along veins, grain boundaries, and along pre-existing deformation bands related to the pseudotachylyte formation event (Fig. 1d; Supplementary Figs. 3–7). Systematic cross-cutting relationships indicate that the serpentinization event post-dates the pseudotachylyte formation, as revealed by the occurrence of serpentine veins and pervasive serpentinization replacing both the pseudotachylites and the host peridotite (Fig. 1c). Microstructural relationships enabled constraints to be placed on the high-pressure serpentinization paths, with spinel and pyroxenes being replaced first, followed by olivine (Fig. 1e; Supplementary Fig. 7). Spinel is replaced by magnetite and chlorite in all samples, including those showing little degrees of serpentinization (Supplementary Figs. 7, 9 and 10). Pyroxenes appear partially to fully replaced by diopside + brucite + antigorite + magnetite ± metamorphic olivine (Supplementary Fig. 7). Metamorphic olivine (Fo\(_84\)) was also found together with antigorite in cross-fibre veins in samples from San Petrone (Fig. 1f). In Lanzo, metamorphic olivine and Ti-clinoohumite overgrew fully serpentinized pseudotachylites in association with antigorite and magnetite (Supplementary Fig. 8). Primary olivine was replaced by antigorite, magnetite, ubiquitous awaruite (Fe–Ni alloy), as well as various types of Fe and Ni sulfides (Fig. 2). Some samples are extremely rich in awaruite. In partially serpentinized samples, awaruite replaces magnetite, whereas in more intensively serpentinized samples magnetite rims around awaruite are found. Awaruite was also found in late lizardite veins replacing relict olivine. Tiny Ir–Os alloys were identified in samples from Monte San Petrone (Fig. 2d).

Microstructural features in partially serpentinized samples, such as delicate antigorite growth on primary olivine and antigorite cross-fibre veins cross-cutting the rock (Fig. 1c–f), indicate that the main serpentinization event happened in the antigorite stability field, i.e., at \( T \geq 370–400 \) °C and depths \( \geq 40 \) km (1 GPa) according to the estimated pressure–temperature paths in the Alpine belt\(^{29}\). This indicates that the serpentinization of the pseudotachylyte-bearing peridotites happened near peak metamorphic conditions in the blueschist-facies Cima di Gratera units (\( T \) climax \( \sim 430 \) °C/1.5 GPa, \( \sim 40–60 \) km depth), between 370 and 400 °C/1 GPa (isograd of antigorite-dominated serpentinites\(^{29}\), \( \sim 40 \) km depth) in the eclogite-facies Lanzo units, and 530–620 °C/2–2.5 GPa (metamorphic peak; \( \sim 80–90 \) km depth) in the Monte San Petrone units\(^{40,42}\).

Redox and fluid chemistry of high-pressure serpentinization. The presence of awaruite in the studied samples indicates \( fO_2 \) conditions lower than the quartz–magnetite–fayalite (QFM) buffer\(^{43,44}\). Overgrowth of awaruite on early magnetite suggests that the \( fO_2 \) decreased during high-pressure serpentinization. Then magnetite growth on awaruite also suggests successive increase in \( fO_2 \) during the same serpentinization event\(^{7}\). These redox patterns during progressive serpentinization are similar to those recorded by low-temperature, low-pressure serpentinization\(^{45}\) and support the potential for high-temperature, high-pressure serpentinization to generate reducing fluids. The compositions of fluid inclusions in the rocks provide additional constraints on the reducing conditions during the high-pressure serpentinization event. Relict olivine commonly contains fluid inclusion trails that propagate from antigorite-filled...
fractures into the olivine (Fig. 3), constraining their formation to the high-pressure serpentinization event. MicroRaman spectroscopy of fluid inclusions reveals the presence of species characteristic of very low fO2 such as ubiquitous methane (CH₄; 2917 cm⁻¹) and H₂ (4156 cm⁻¹) (Fig. 3d–g). Ethane (C₂H₆), hydrogen sulfide (H₂S), dinitrogen (N₂), ammonia (NH₃), and possibly another N–H compound (3422 cm⁻¹) were detected in some fluid inclusions, yet not ubiquitously (Fig. 3d–f, Supplementary Note 4).

Neither H₂O nor CO₂ was detected in the fluid inclusions. Nevertheless, the initial presence of H₂O in the fluid inclusions is indicated in some samples by the occurrence of hydrous step-daughter minerals inside the inclusions such as lizardite and brucite (Fig. 3d–g). The absence of a water-vapour Raman signal in fluid inclusions free of hydrous step-daughter minerals suggests either that thin films of H₂O are present in some fluid inclusions, but are not detectable by MicroRaman spectroscopy⁴⁶, or that syn-entrapment of immiscible H₂O-free and H₂O-fluids

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**Fig. 3 H₂-CH₄-rich fluid inclusions.** a–c Photomicrographs of olivine-hosted fluid inclusions (FI) in partially serpentinized pseudotachylyte-bearing peridotites. Note the presence of the fluid inclusions along secondary trains propagating from serpentinized cracks and cross-cutting the primary olivine (a, b), suggesting their formation during the serpentinization events. d–g MicroRaman spectra of the fluid inclusions shown in a–c. The spectrum of the host olivine (g) is shown for reference. Note the presence of CH₄ and H₂ also in fluid inclusions free of daughter minerals, suggesting that the initial fluid trapped in the inclusions was already reduced. See Supplementary Fig. 13 for additional details. Scale bars: a, b 50 μm; c 20 μm.
occurred. The latter hypothesis has been observed in natural samples and experimentally at pressure–temperature conditions consistent with our case studies26,47,48. The abundance of CH4 in olivine-hosted fluid inclusions indicates that carbon was present in the serpentinizing fluid and was converted to CH4 during the serpentinization event. Graphitic C was sporadically detected in some fluid inclusions in samples from Lanzo (Fig. 3d), and most likely reflects post-entrapment re-speciation inside the fluid inclusions.

The microstructural association of antigorite and mineral and fluid species classically attributed to low-oxygen conditions, such as awaruite, H2 and CH4, indicates that reducing conditions and genesis of H2 and CH4 were achieved during the high-pressure serpentinization event at temperatures ≥400 °C. The presence of CH4 and H2 in fluid inclusions free of post-entrapment serpentinization (Fig. 3f) suggests that these species were present in the fluid during the entrapment. The non-systematic occurrence of step-daughter minerals inside the fluid inclusions also excludes the possibility that the reduced fluid species were generated through serpentinization inside the fluid inclusions, as proposed in samples from low-temperature environments49. Nevertheless, the presence of step-daughter minerals potentially bearing ferric iron such as lizardite suggests that post-entrapment serpentinization and additional H2 and CH4 production may have occurred at lower temperatures inside the inclusions during exhumation. The latter hypothesis is supported by the occurrence in the host rock of lizardite veins containing low fO2 minerals such as awarute (Fig. 2c).

We performed thermodynamic calculations with the deep earth water (DEW) model50 in order to constrain the mineralogical, fluid, and redox patterns of high-pressure serpentinization (Fig. 4) (Methods and Supplementary Note 3). We assumed that the fluid responsible for the serpentinization of the pseudotachylite-bearing peridotites was initially equilibrated with the surrounding serpentinite consisting of antigorite + magnetite + brucite + chlorite + olivine in the system Na–Ca–Fe–Mg–Al–Si–Cl–S–O–H(±N). This fluid was then reacted with a peridotite of harzburgitic composition (olivine + clinopyroxene + orthopyroxene + spinel; Ca–Mg–Fe–Al–Si–O system) over a range of pressures, temperatures, and water-rock ratios relevant to subduction zones. The fO2 of the infiltrating fluid was buffered at QFM, with CH4 concentrations being 1 to 3 orders of magnitude lower than CO2 (Methods and Supplementary Table 2). The calculations were carried out for fluid/rock ratios ranging from 1 to 10.

Figure 4 shows the mineralogical evolution of an harzburgite interacting with a carbonate-undersaturated fluid at 400 °C and 1 GPa, i.e., approximately corresponding to the conditions of the antigorite serpentinization event in the selected blueschist-facies natural samples from the Cima di Gratera. It can be seen in Fig. 4 that the reaction proceeds by progressively transforming spinel, clinopyroxene, orthopyroxene, and olivine, consistent with the microstructural features observed in the natural samples. Magnetite starts to form during the early stages of the reaction along with chlorite, followed by diopside, and antigorite. At reaction completion, the calculations show that serpentinization reached about 50 vol% for a fluid/rock ratio equal to 1. Complete serpentinization at 400 °C and 1 GPa was obtained for fluid/rock ratios >5 (Supplementary Table 3). Metamorphic olivine is predicted to form in equilibrium with antigorite (Supplementary

![Fig. 4 Thermodynamic modelling of high-pressure serpentinization of harzburgite and related redox evolution and H2 concentrations.](https://doi.org/10.1038/s41467-020-17342-x)
Table 3), as observed in the natural samples (Fig. 1e, f; Supplementary Figs. 7 and 8).

Reacting fluids equilibrated with a carbonate-bearing serpentinite result in higher degrees of serpentinization for a given fluid/rock ratio (Supplementary Table 3). This suggests that aqueous fluids equilibrated with carbon-rich rocks, e.g., metasedimentary rocks, may boost peridotite serpentinization at high-pressure conditions. This effect diminishes with increasing temperature. At 1 GPa and 400 °C, the fO2 strongly decreases during the reaction process as a result of magnetite formation (Fig. 4b). The highest reducing potential is observed for partially serpinitzed assemblages, while calculations reaching full serpentinization show lesser decrease in fO2, as documented for low-pressure serpentinization55. At 1 GPa, the lowest fO2 is predicted at 400 °C (Fig. 4c). At these conditions, the H2 concentration in the fluid reaches about 40 mmol/kg and decreases for serpentinization degrees >50% (Supplementary Table 4).

At temperatures lower than 500 °C, the carbon-bearing fluid species are dominated by CH4, which is seven orders of magnitude more abundant than CO2. At higher temperatures (>500 °C), the degree of serpentinization decreases progressively, thus lowering the production of magnetite and H2. As a consequence, fO2 progressively increases towards QFM from below (Fig. 4) and higher concentrations of CO2 over CH4 are predicted (Supplementary Table 4). The CH4 concentration is dependent on the initial carbon content of the infiltrating fluid. For infiltrating fluids in equilibrium with a carbonate-bearing serpentinite, the CH4 concentrations during serpentinization reaches 19 mmol/kg at 1 GPa and 400 °C. For reference, CH4 concentrations in serpentinite-hosted vents along mid-ocean ridges reach 2.5 mmol/kg9. At 1 GPa, temperature increasing over 450 °C results in lower degrees of serpentinization for a given fluid/rock ratio, and thereby less of a decrease in fO2 and lower H2 and CH4 concentrations in the fluid (Fig. 4c). At 500 °C and 1 GPa and fluid/rock ratio = 1, the amount of magnetite coexisting with antigorite drastically decreases of about two orders of magnitude relative to temperatures <500 °C and the fO2 remains at QFM (Supplementary Table 3). Calculations at 2 GPa indicate that serpentinization of ultramafic rocks at depth consistent with eclogite-facies conditions is still effective at ~500 °C and forms about one order of magnitude more magnetite relative to the same temperature at 1 GPa. With increasing pressure, the concentration of H2 did not linearly follow the degree of serpentinization and the fO2 as a result of the strong decrease in solubility of gaseous H2 with pressure. The modelled nitrogen speciation matches the fluid inclusion data, with NH3 being the dominant N-species in equilibrium with a serpentinized peridotite at 1–2 GPa (Supplementary Table 4).

The calculations also show that pressure favours the formation of higher amounts of metamorphic olivine in equilibrium with antigorite and magnetite at lower temperatures (Supplementary Table 3). Based on the modelled metamorphic olivine compositions, serpentinization of the San Petrone pseudotachylites took place at ~500 °C and 1–2 GPa, which are in agreement with the metamorphic evolution of this unit.

Subduction-zone sources of deep H2 and abiotic CH4. Our study provides evidence that high-pressure serpentinization can take place at the expense of subducted fresh mantle rocks at blueschist-to-eclogite-facies conditions. Free water circulation in subducted mantle sections is predicted by numerical models31 and can promote high-pressure serpentinization. Our results show that this process is accompanied by Fe oxidation and generation of high concentrations of H2 and CH4 in the resulting fluids. We found that the fO2 of the fluids produced by high-pressure serpentinization can be up to 4 log units lower than in subducted oceanic serpentinites52 (Fig. 4). This provides a new and complementary view on the role of serpentinite and serpentinization on the redox state of subducting slab fluids, which have generally been considered rather oxidized19,20,35. Considering the potentially large volumes of peridotites being subducted annually, this process may strongly affect the redox of subduction-zone fluids and the mobility of deep C compared to more oxidized fluids54.

At the temperatures in subduction zones that we considered, high-pressure serpentinization produces favourable conditions for overcoming the kinetic inhibition of the abiotic conversion of dissolved carbon into CH4 in marked contrast to shallower, lower temperature environments55,56. Moreover, the presence of catalysts such as Fe-Ni and platinum-group alloys, here shown to be widespread in serpentinized ultramafic rocks formed at high pressures, could greatly enhance the kinetics of CO2 hydrogenation to CH457. At even greater depths in subduction zones, where serpentinites dehydrate, there is also the potential for these rocks to release reduced fluid species such as H2, CH4, and H2S52. We suggest that these strongly reduced fluids may be preserved during up-slope migration through subducted mantle sections (Fig. 3). Percolation of these fluids through more oxidized subducted oceanic crustal and sedimentary lithologies may result in conversion of CH4 into graphitic C or carbonate minerals into less reduced C-bearing fluid species (e.g., CO, HCOOH, CO2, or HCO3–), or may promote reduction of carbonate-bearing lithologies and additional CH4 generation58,59.

Although large uncertainties still exist regarding the definition of serpentinization patterns in the mantle wedge above subducting slabs, several examples of inferred high-pressure, mantle-wedge serpentinized peridotites exhibit mineral assemblages comparable to the samples presented in this study60,61. Therefore, our petrological data and thermodynamic modelling can be extrapolated to portions of the hydrated mantle wedge above subducting slabs24,30, where variable degrees of high-pressure serpentinization occur along more than 55,000 km of forearc mantle domains24. Emissions of H2 and CH4 have been identified in the Izu-Bonin-Mariana subduction and ascribed to the serpentinization of the shallow forearc mantle to depths potentially reaching 27 km13. Our study suggests that the source areas and magnitudes of H2–CH4–rich fluids at convergent margins may be much deeper and much larger, respectively, than previously expected.

Our data enable provisional estimates of high-pressure H2 and abiotic CH4 release from worldwide subduction zones. Considering extents of serpentinization ranging from ~10 to ~45%, consistent with predictions of mantle-wedge serpentinization worldwide24 (Supplementary Note 3), the highest and lowest H2 production through antigorite serpentinization are expected at 1 GPa (~35 km depth) and 400 °C (~0.3 kg H2 per m3 of rock) based on the instantaneous H2 concentration at reaction completion), and 2 GPa (~70 km depth) and 500 °C (9 × 10–3 per m3 of rock), respectively (Fig. 4d; Supplementary Table 4). Using these instantaneous concentrations as conservative values for the H2 production during serpentinization, it is estimated that the minimal annual production of H2 from high-pressure serpentinization of the mantle wedge lies between 9 × 10–3 and 0.3 Mt (Supplementary Note 3). Variations in the reactiv peridotite and fluid compositions may result in additional heterogeneity. The associated release of CH4 can greatly vary as a function of parameters such as the concentration of C in the serpentinizing metamorphic fluids, the kinetics of the hydrogenation reaction, and the presence of catalysts. For example, from ~35 to 70 km depth (1–2 GPa) and temperature of 400–550 °C and infiltrating fluid ranging from largely carbonate-
undersaturated to carbonate-saturated, the annual CH₄ production through partial serpentinization of the mantle wedge could be in the range of 2.3 × 10⁻³ to 1.0 Mt (Supplementary Note 3). These numbers would be greatly increased by considering the cumulative H₂ production instead of an instantaneous concentration, higher C concentrations, and additional fluxes from lizardite serpentinization in the mantle wedge (<35 km depth), from slab-serpentinization and from post-entrapment serpentinization of aqueous fluid inclusions in high-pressure ultramafic rocks, and from serpentinite dehydration.

Global estimates of geological abiotic H₂ and CH₄ production vary widely. Serpentinization at mid-ocean ridges is a major source of these gases in the Earth’s lithosphere, with H₂ and CH₄ production reaching ~0.02–1.4 and ~1.1–1.9 Mt/y, respectively. Global estimates for shallow forearc serpentinization and ophiolite formations are not available to date. High-pressure serpentinization in subduction zones is currently not included in the global inventory of geological abiotic H₂ and CH₄ sources. However, our results and preliminary estimates on high-pressure serpentinization are consistent with—and may potentially exceed—the range of H₂ and CH₄ production proposed for mid-ocean ridges. We therefore propose that deep serpentinization of slab and mantle-wedge ultramafic rocks may represent the largest source of natural energy in the form of H₂ and abiotic CH₄ in Earth’s lithosphere. In warm subduction zones, mantle-wedge serpentinization and the resulting integrated H₂ and CH₄ fluxes are maximized but limited to shallower depths compared to cold subduction zones. High integrated H₂–CH₄ fluxes from the mantle wedge are expected for thermal gradients characteristic of Neoarchean to Cambrian subduction (Supplementary Note 4), even though the possibility for deep serpentinitization reactions to have occurred in early subduction systems is not an established feature. Nevertheless, similar warm geothermal gradients are predicted in active convergent margins such as Cascadia (Supplementary Fig. 12). In cold subduction zones characteristic of the Phanerozoic, high-pressure serpentinization may have extended to greater depths compared with warm subduction zones but is predicted to be less pervasive at least in the mantle wedge. However, because the concentration of H₂ and CH₄ is higher in fluids in equilibrium with partially serpentinized rocks compared to strongly serpentinized ones, it is expected that mantle-wedge domains in cold subduction zones bear the greatest potential to produce deep, highly concentrated H₂–CH₄ fluids.

Nitrogen and ammonia in deep serpentinization fluids. Nitrogen enters subduction zones mainly as organic nitrogen present in sedimentary organic matter and ammonium ions (NH₄⁺) bound in phyllosilicates. Prograde dehydration of these minerals is expected to release nitrogen, with N₂ being considered the dominant dissolved N-bearing species in subduction fluids. In this study, nitrogen-bearing species were identified in fluid inclusions from several samples (Fig. 3f, Supplementary Fig. 13). Subducting slabs, especially subducted sedimentary rocks, host orders of magnitude more nitrogen than mantle rocks. Nitrogen species have not been documented in CH₄-bearing fluids inclusions in ultramafic rocks from mid-ocean ridges, shallow forearc settings, and ophiolites. The involvement of fluids released by dehydration of subducted sediments in the process of high-pressure serpentinization, however, may explain the nitrogen-rich fingerprints observed in our samples relative to shallower settings. The presence of abundant nitrogen in fluid inclusions may therefore help to differentiate between CH₄-bearing fluids generated by serpentinitization at mid-ocean ridges and shallow settings relative to the equivalent gases produced through high-pressure serpentinization. Additionally, the abundance of nitrogen in fluid inclusions may help to identify the source of serpentinizing fluids at high-pressure conditions.
The identification of NH₃ in the studied fluid inclusions provides new perspectives on the chemistry of high-pressure metamorphic fluids in subduction zones. Ammonia in geological fluid is mainly produced through biological and thermal degradation of organic matter. The formation of NH₃ in the rocks we studied, however, was likely related to the strongly reducing conditions achieved abiotically during high-pressure serpentinization that stabilized NH₃ over N₂ in the fluid, as predicted by the thermodynamic modeling results (Supplementary Table 4). To the best of our knowledge, our study represents the first documentation of NH₃ in metamorphic fluids at concentration levels detectable by MicroRaman spectroscopy68. The genesis, preservation, and evolution of NH₃ in metamorphic fluids may provide new insights on the cycle of nitrogen in subduction zones. Ammonia can be a powerful ligand for transition metals in geologic fluids69. The presence of platinum-group elements particles as well as abundant alloys in the studied samples (Fig. 2d) suggests that deep serpentinization reactions and genesis of NH₃ may represent a potential pathway for the transport of transition metals in subduction zones. The re-distribution of NH₃ into nitrogen species with weaker ligand properties can therefore control the deposition of transition metals at convergent margins. Thermal decomposition of NH₃ to N₂ in the presence of catalysts may also represent an additional source of natural H₂ (2NH₃ → N₂ + 3H₂)69. Oxidation of NH₃ can lead to the formation of N₂ and H₂O69. The conversion of NH₃ to N₂ also represents an important step in the evolution of nitrogen isotopic signatures of deep geological fluids70.

The circulation and transformation of deep NH₃-bearing fluids may also play an important role in sustaining the deep subsurface biosphere at shallower depths (see next section). Last, the identification of NH₃ in fluids generated by the alteration of ultramafic rocks at high-pressure, low-temperature conditions may provide insights on the evolution of other planetary interiors. As an example, accreted NH₃ is proposed to have played an important role in the evolution of Titan's atmosphere71. Interestingly, Titan's core pressure and temperature conditions may overlap with the conditions investigated in mantle rocks in this study72, suggesting that cold subduction zones on Earth may provide a possible new terrestrial analogue for planetary science studies.

Discussion

Reduced fluid species such as CH₄, H₂, H₂S, and NH₃ are key compounds in planetary evolution, prebiotic chemistry, and metabolism73,74. The release of such reduced fluid species from subducting slabs is generally considered to happen at relatively low temperature and pressure conditions through biotic/thermogenic process related to the recycling of subducted biogenic substances75,76 (Fig. 5). At the higher pressure–temperature conditions characteristic of subduction-zone metamorphism, more oxidized conditions are traditionally expected20. The results presented in this study, however, show that fluids highly concentrated in such compounds can be formed abiotically down to 40–80 km depth through high-pressure serpentinization, potentially in high amounts, and along thousands of km at convergent plate boundaries (Fig. 5). These processes occur way outside the parameter space for deep life77. However, the migration of these fluids towards shallower depths within the limits of the deep subsurface biosphere may have important implications for the sustainment of deep microbial communities at convergent margins (Fig. 5). While a growing body of literature has highlighted the global role of the subsurface biosphere in contributing to the deep carbon cycle78, relatively few studies have so far investigated the deep subsurface communities in subduction zones79,80, and to what extent this deep life depends on deeper carbon recycling at convergent margins2.

Although the possibility that reducing high-pressure fluids could migrate and eventually reach the deep subsurface biosphere remains poorly constrained, and could be the subject of future studies, the geological conditions at which this migration could occur strongly support this hypothesis. The hydrating mantle wedge would in fact represent an ideal means to maintain the reduced state of these fluids during upward migration80 before crustal recycling. Relative to CO₂-rich fluids, which are expected to promote carbonate precipitation in mantle-wedge peridotites80,82 and at shallower depths into the crust13, reduced CH₄-rich fluids should not promote the same reactions. Possible exceptions are additional serpentinization reactions—and thereby additional reducing potential—and graphite precipitation. Cooling of these metamorphic fluids makes CH₄ thermodynamically more stable relative to CO₂75. This suggests that the preservation of CH₄ formed through high-pressure serpentinization is enhanced during upslope migration in the forearc (Fig. 5). Moreover, when the fluids reach temperatures less than about 400 °C, conditions that represent large portions of forearc mantle wedges, CH₄ may be kinetically inhibited from reaction as has been suggested for decades75,78,81. Kinetic inhibition of CH₄ reactivity would therefore be expected to result in a state of metastable equilibrium in the fluid in which the relative stabilities of many aqueous organic species (e.g., formate and acetate) are greatly enhanced, offering an ideal opportunity for support of an opportunistic microbial community.

Recent discoveries strongly suggest that deep subsurface microbial communities present in the forearc and arc continental crust respond to deeply sourced carbon and volatile species2,3. In particular, the study by Barry et al.2 carried out in the Costa Rica convergent margin identified significant differences in the starting composition of the carbon end-members feeding into their geological precipitation sink, and propose that these differences are directly related to primary differences in the carbon species released from the subducting slab. Most relevant to this discussion, the signature of slab fluids was visible throughout the forearc and into the volcanic front. This suggests pervasive migration of fluids from the subducting slab thorough the mantle wedge into the overlying forearc crust where they finally interact with the subsurface biosphere. During the fluid migration towards the pressure–temperature range suitable for life to flourish82, it is plausible that the reduced species identified in this study, e.g., CH₄, H₂, NH₃, and H₂S, encounter more oxidized redox couples therefore fueling deep subsurface life metabolic reactions78,83. Possible oxidants include CO₂, Fe³⁺ present in the more oxidized crustal rocks, partially oxidized organic carbon and halogenated compounds from diageneric processing of surface-derived organic matter, as well as oxidized sulfur and nitrogen species derived from the entrainment of surface and meteoric waters into deep hydrothermal systems at convergent margins75. Possible microbial metabolic strategies supported by the ascent of reduced metamorphic fluids include methanogenesis, anaerobic methane oxidation potentially coupled to a variety of oxidases77 as well as a variety of exergonic catabolic strategies. Anaerobic methane oxidation is generally coupled to sulfate reduction13,84, but it has been recently linked also to NO³⁻ and MnO reduction85,86 and can theoretically be coupled to other electron acceptors including Fe³⁺ and zerovalent sulfur3. Members of microbial taxa known to carry out these reactions have been reported in several continental subsurface ecosystems78. Additionally, H₂O, CO, and NH₃ found to be abundant in the deep metamorphic fluids in this study might fuel widespread chemolithoautotrophy as recently reported at convergent margins75,82 and other subsurface continental settings87. Heterotrophic and fermentative members

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of the community commonly reported in other continental settings\(^5,9,8\) may be supported by the aequous organic species resulting from abiotic synthesis (e.g., formate and acetate\(^8\)). Overall, the presence of a large supply of reduced volatile species has the potential to support diverse microbial assemblages at convergent margin.

Despite the large predicted flux, the surface emissions of similar deeper fluids released by high-pressure serpentinization, however, may not be obvious, owing to the reworking by oxidative fluid–rock interactions and microbial activity within the crust. A similar overprint of geochemical and biological factors has been shown to mask potentially large carbon fluxes in the Costa Rica convergent margin\(^2\). Abiotic and biogenic recycling of high-pressure CH\(_2\) and associated reduced compounds should therefore be considered in the interpretation of forearc volatile signatures and in the inventory of deep carbon processes.

Overall, in light of recent investigations into the role of subsurface microbes at convergent margins\(^3,17\), our results suggest that high-pressure serpentinization is potentially an important source of reduced volatiles to the deep subsurface biospheres of convergent margins. Considering that low temperature and pressure serpentinization also takes place at subduction zones in the shallow forearc mantle and in obducted ophiolites, we propose that convergent margins may have represented the major source of H\(_2\) and abiotic CH\(_4\) from different depths to the surface biosphere. The identification of these different sources within the subsurface biosphere represents an important challenge for future work.

**Methods**

**Sample preparation and microanalysis.** Samples from the Cima di Gratera, Monte San Petrone, and Lanzo were studied by optical microscopy, scanning electron microscopy, and energy dispersive X-ray analysis (SEM-EDX), electron microprobe, and Raman spectroscopy.

For each sample, a 30-μm-thick polished thin section was prepared. For all samples containing fluid inclusions but one (OF5223), a 100-μm-thick bi-polished thin section was also prepared to avoid potential contaminations (e.g., by epilam).

The thin sections selected for electron microscopy and microprobe were carbon-coated. MicroRaman analyses were conducted prior to C coating or on uncoated thick sections.

SEM-EDX analyses were performed with a Zeiss Ultra 55 field emission gun (FEG) SEM at IMPMC. The analyses were done with a working distance of 7.5 mm and operated at 15 kV with a 120 μm aperture. Backscattered-electron mode was used to investigate chemical heterogeneities using an Angle Selective Backscattered Detector (AsB) or an Energy Selective Backscattered Detector (EsB). Energy dispersive X-ray spectrometry (EDXS) maps were acquired using an EDXS QUANTAX system equipped with a silicon drift detector XFlash 4010 ( Bruker).

Data were processed with the software Esprit (Bruker).

Mineral chemistry was determined by wavelength-dispersive spectrometry using a JEOL JXA 8200 Superprobe at the Institute of Geological Sciences (University of Bern). Analytical conditions included 15 keV accelerating voltage, 20 nA sample current, 40 s dwell times (including 2 × 10 s of background measurements), and a beam diameter of 2 μm. Higher current and larger beam size were used for spinel measurements (50 nA and 5 μm). For silicate minerals, nine oxide compositions were measured, using synthetic and natural standards: wollastonite (SiO\(_2\)), anorthite (Al\(_2\)O\(_3\)), wollastonite (CaO), almandine (FeO), olivine (MgO), calcite (CO\(_2\)), pyroxene (MgO), bunsenite (NiO), rutile (TiO\(_2\)), and spinel (CrO\(_2\)). For oxides, measurements were made using synthetic standards: hematite, magnetite, and fayalite buffer. The hematite buffer was never observed, indicating that FeO conditions never exceeded the hematite–magnetite buffer. Nevertheless, it is worth noting that the chosen initial fluid \(fO_2\) does not affect the final \(fO_2\) condition at equilibrium after fluid–rock interaction. Choosing higher initial \(fO_2\) condition will only lead to higher \(fO_2\) (Fig. 4c in the main text), thus our initial \(fO_2\) conditions give more conservative results.

The moality of carbon in the fluid was set at values between 0.001 and 0.05, which encompass the values of carbon moality for in equilibrium with carbonate–silicate–fluid assemblage at 400–500 °C and 1–2 GPa based on the EQ3 calculations. EQ6 was then used to model the interaction between the EQ3 fluid and a harzburgite assemblage consisting of olivine, orthopyroxene, clinopyroxene, and spinel. The composition of the main solid solutions in the EQ3 and EQ6 calculations were set based on the mineral compositions analysed in the samples. Fluid/rock ratios from 1 to 10 were considered.

**Data availability**

The main data generated during this study are available in Supplementary Tables 1–4. Additional information is available from the corresponding author on request.

**Code availability**

The code used for thermodynamic modeling is available at http://www.dewcommunity.org.

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**Thermodynamic modelling**

High-pressure serpentinization was simulated with the DEW model\(^9\) and the EQ3/EQ6 software\(^8\) with a modified Berman thermodynamic database\(^9\) (see also Supplementary Note 3 for additional information and discussion). Firstly we calculated with EQ3 the composition of a fluid in equilibrium with a serpentinite assemblage consisting of antigorite + magnetite + brucite + chlorite + olivine, which best represents the general mineralogical composition of serpentinites at blueschist-to-eclogite-facies conditions\(^9,39\). The \(fO_2\) of the equilibrium was set at QFM (quartz–fayalite–magnetite buffer). The initial value of the fluid \(fO_2\) was chosen on the basis the predicted \(fO_2\) conditions for a fluid equilibrated with the assemblage antigorite + magnetite + olivine + brucite + by Piccoli et al.\(^52\). In our oceanic serpentinite samples hematite was never observed, indicating that \(fO_2\) conditions never exceeded the hematite–magnetite buffer. Nevertheless, it is worth noting that the chosen initial fluid \(fO_2\) does not affect the final \(fO_2\) condition at equilibrium after fluid–rock interaction. Choosing higher initial \(fO_2\) condition will only lead to higher \(fO_2\) (Fig. 4c in the main text), thus our initial \(fO_2\) conditions give more conservative results.

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Author contributions
A.V.B. designed the project, collected and interpreted samples and data, and wrote the paper. D.A.S. participated in the thermodynamic modeling and wrote the paper. F.P. collected part of the data and wrote the paper. F.R. collected part of the data. I.D. and D.G. wrote the paper.

Competing interests
The authors declare no competing interests.

Additional information
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