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Methane genesis within olivine-hosted fluid inclusions in dolomitic marble of the Hida Belt, Japan

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Abstract

Abiotic synthesis of hydrocarbon-bearing fluids during geological processes has a significant impact on the evolution of both the Earth's biosphere and the solid Earth. Aqueous alteration of ultramafic rocks, i.e., serpentinization, which forms serpentinite, is one of the geological processes generating abiotic methane (CH_4). However, abiotic CH_4 generation is not limited to the serpentinization of mafic and ultramafic lithologies. Metasedimentary dolomitic marble from the Hida Belt, Japan, is characterized by the presence of forsterite-rich olivine ($Fo_{\sim 89-93}$), and olivine crystals contain abundant fluid inclusions (<1 to 10 μm in size). Raman spectroscopic analyses of olivine-hosted fluid inclusions found that both primary and secondary fluid inclusions contain CH_4, lizardite/chrysotile, and brucite. This indicates that micro-scale interactions between COH fluid and host olivine produced CH_4 through the reduction of CO_2 by H_2 released during local serpentinization within inclusions. Our observation implies that the dolomitic marble has the potential to be a key lithology for the synthesis and storage of abiotic CH_4 in a shallower crustal portion of orogenic belts.

Keywords Dolomitic marble, Fluid inclusion, Olivine, Abiotic methane synthesis, Hida Belt

1 Introduction

Serpentinization of ultramafic rocks is one of the most common abiotic methane (CH_4) generation processes. The process involves the oxidation of ferrous iron contained in primary olivine to ferric iron in secondary minerals, such as serpentine, brucite, and magnetite. Consequently, this oxidation leads to the generation of hydrogen (H_2)-bearing reduced fluids, and the production of CH_4 during serpentinization results from the reduction of CO_2 by these H_2-bearing fluids (e.g., McCollom and Bach 2009; Sleep et al. 2004; Suda et al. 2014). In the natural environment, the presence of hydrocarbon-bearing serpentinite-related fluids has been observed at seafloor hydrothermal fields and ophiolites (e.g., Kelley et al. 2005; Miller et al. 2016; Proskurowski et al. 2008). Although it has been known that shallow low-temperature serpentinization generates H_2-bearing reduced fluids (e.g., Etiope et al. 2011; Etiope and Sherwood Lollar 2013; Kelley et al. 2005; Mottl et al. 2003; Ohara et al. 2012; Proskurowski et al. 2008), Evans (2010) showed that deep high-temperature and high-temperature serpentinization forming antigorite does not generate H_2-bearing reduced fluids. Nevertheless, recent natural observations revealed that high-temperature serpentinization enables the generation of reduced fluids (Boutier et al. 2021; Vitale Brovarone et al. 2020; Zhang et al. 2021). Recent studies have reported abiotic CH_4 synthesis in subduction zone lithologies (Spránitz et al. 2022; Tao et al. 2018; Wang et al. 2022); CH_4-rich fluid inclusions in omphacite from carbonated eclogite of SW Tianshan, China are

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considered to be formed by the redox reactions of Fe-bearing carbonates in water (Tao et al. 2018; Wang et al. 2022). Abiotic CH_4 synthesis in such lithologies is rare, and serpentinization has attracted interest as a major abiotic CH_4 production process. However, as reported in this study, abiotic CH_4 production during serpentinization is not limited to the ultramafic lithologies found in abyssal peridotite and ophiolite. Reconnaissance studies for the abiotic CH_4 production in supracrustal metasedimentary rocks in the continental crust have just begun.

In this paper, we present the occurrence of olivine-hosted fluid inclusions containing CH_4 from a dolomitic marble from the Hida Belt, Japan. Based on the mineral inclusions associated with those fluid inclusions, we propose that abiotic CH_4 synthesis in fluid inclusions is not limited to ultramafic lithologies but also occurs in non-ultramafic lithologies within the middle crustal section of the continental margin.

2 Geological background

The Hida Belt of central Japan (Fig. 1a, b) is a continental fragment, which was once a part of a crustal basement of the East Asian continental margin prior to the back-arc opening of the Japan Sea in the mid-Miocene (e.g., Isozaki et al. 2010, 2023). It consists mainly of Permo-Triassic granite-gneiss complexes with Jurassic granitic intrusions. The metamorphic lithologies of the Hida Belt are mainly of granitic gneiss, amphibolite, marble, calcareous gneiss, quartzofeldspathic gneiss, and minor pelitic gneiss (cf., Ehiro et al. 2016). The timing of the upper amphibolite- to granulite-facies regional metamorphism has been dated as ~260–230 Ma (e.g., Cho et al. 2021; Horie et al. 2018; Takahashi et al. 2018).

In the Hida Belt, a large amount of metacarbonate rocks occur accompanying gneissose rocks (Kano 1998). The protolith has been regarded to be continental platform carbonates (e.g., Isozaki 1996, 1997; Sohma and Kunugiza 1993). The sedimentary origin of the metacarbonate rocks is supported by their C–O–Sr isotope compositions (Harada et al. 2021b). Most of the metacarbonate rocks in the Hida Belt consist mainly of calcite (i.e., calcite marble) with a minor amount of clinopyroxene, quartz, and titanite, whereas dolomitic marble which consists mainly of Mg-rich calcite and dolomite is rare (e.g., Harada et al. 2021b; Kano 1998). The calcite–dolomite solvus thermometry from calcite–dolomite intergrowth in dolomitic marble gives a temperature of ~600 °C (Imai et al. 1977; Kano 1998).

3 Analytical methods

Micro Raman spectroscopic analyses were performed to characterize fluid inclusions. Unpolarized Raman spectra were obtained by a laser Raman spectrometer, the HORIBA Jobin Yvon LabRAM300 at Tohoku University, connected to a 1024 × 256-pixel charge-coupled device (CCD) detector. The measurements used a 488 nm solid-state laser with a confocal hole of 200 μm, a slit width of 100 μm. The laser was focused through an Olympus MPlan 100 × objective lens (N.A. = 0.9). The laser output was 25 mW at the source and approximately 5.0 mW at the sample surface. The laser spot size was approximately 1 μm. Grating with 600 lines/mm and 1800 lines/mm was used for analyses. The spectral resolution is ~5 cm^{-1} for 600 lines/mm grating and ~2 cm^{-1} for 1800 lines/mm grating. The pixel resolution of this Raman spectrometer when using a grating of 600 lines/mm is 5.5 cm^{-1}/pixel and 4.1 cm^{-1}/pixel at about 1000 cm^{-1} and 3650 cm^{-1}, respectively, and the resolution when using a grating of 1800 lines/mm is 1.8 cm^{-1}/pixel and 1.3 cm^{-1}/pixel at around 1000 cm^{-1} and 3650 cm^{-1}, respectively. Two accumulations of 10–120 s were collected for each spectrum. The calibration of the spectrometer was performed using a Si crystal and a diamond. The spectral baselines were corrected, and the spectra were fitted using the software package PeakFit v4.12 (SeaSolve Software Inc.).

4 Results

4.1 Sample description and petrography

The investigated dolomitic marble samples were collected from an outcrop along the Takahara River, Kamioka area, Gifu Prefecture (Fig. 1a, b). Although the dolomitic marble occurs surrounded by gneissose rocks and leucogranite, the contact between dolomitic marble and surrounding lithologies cannot be observed in the field. The dark-colored partially serpentinized olivine occurs as layers with a variety of widths (up to several tens of centimeters) in white carbonate minerals (Fig. 1c, d). The dolomitic marble exhibits variations in both the modal abundance and grain size of olivines.

The investigated dolomitic marble shows no remarkable foliation and commonly shows granoblastic texture. It consists mainly of Mg-rich calcite, dolomite, and olivine ($Fo_{\sim 89-93}$), with a small amount of tremolite, clinohumite, and phlogopite along with trace apatite (Fig. 2a). Carbonate minerals (calcite and dolomite) occur in a wide range of sizes (up to ~3 mm). The major carbonate minerals of the olivine-rich layer and carbonate-rich part are calcite and dolomite, respectively. Abundant tiny rectangular dolomite crystals were observed in calcite, suggesting the exsolution of dolomite from calcite. Olivine occurs as granular-shaped crystals with a wide range in size (up to ~3 mm). Almost all olivine crystals have partly or completely suffered serpentinization, forming serpentine, brucite, and magnetite (Fig. 2b). Olivine contains calcite, dolomite, and abundant fluid inclusions (Fig. 2c, d). Mesh texture after olivine is commonly observed. Raman

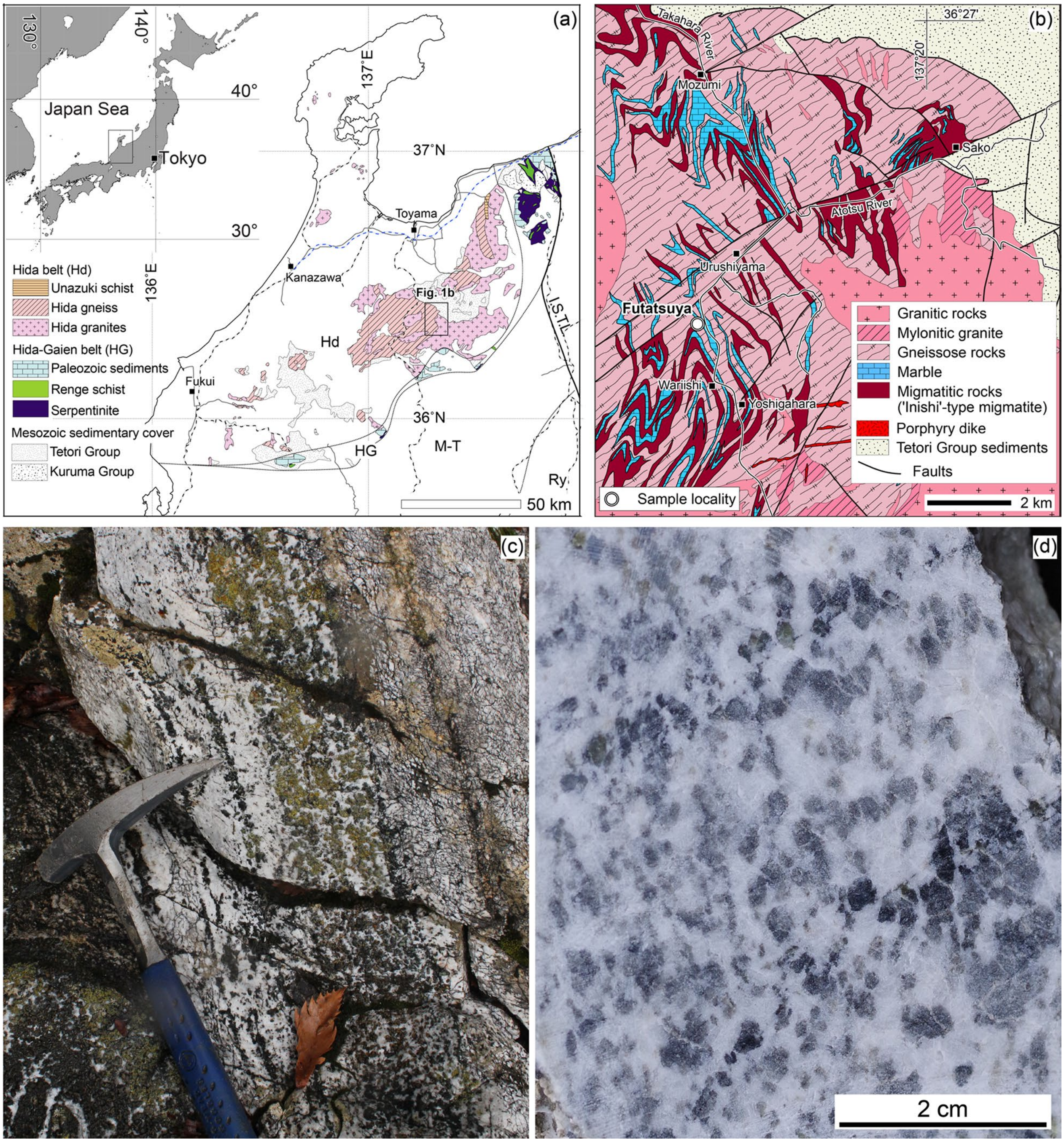

Fig. 1 Geological maps (**a**, **b**) and photographs of investigated dolomitic marble (**c**, **d**). **a** Simplified geological map of the Hokuriku region, showing locations of the Kamioka area (modified after Harada et al. 2021a,b). Hd, Hida Belt; HG, Hida-Gaien Belt; I.S.T.L., Itoigawa–Shizuoka Tectonic Line; M–T, Mino–Tamba Belt; Ry, Ryoke Belt. **b** A geological map of the Kamioka area, showing sample localities (modified after Harada et al. 2021a,b). **c** The field occurrence of the dolomitic marble (Kamioka area, the Hida Belt). **d** A sample slab of dolomitic marble. Black minerals are partially or completely serpentinized olivine

spectroscopic analyses show that the serpentines are lizardite and chrysotile.

4.2 Description of olivine-hosted fluid inclusions

Fluid inclusion analyses were performed on both thin sections and epoxy-mounted olivine crystals. Olivine

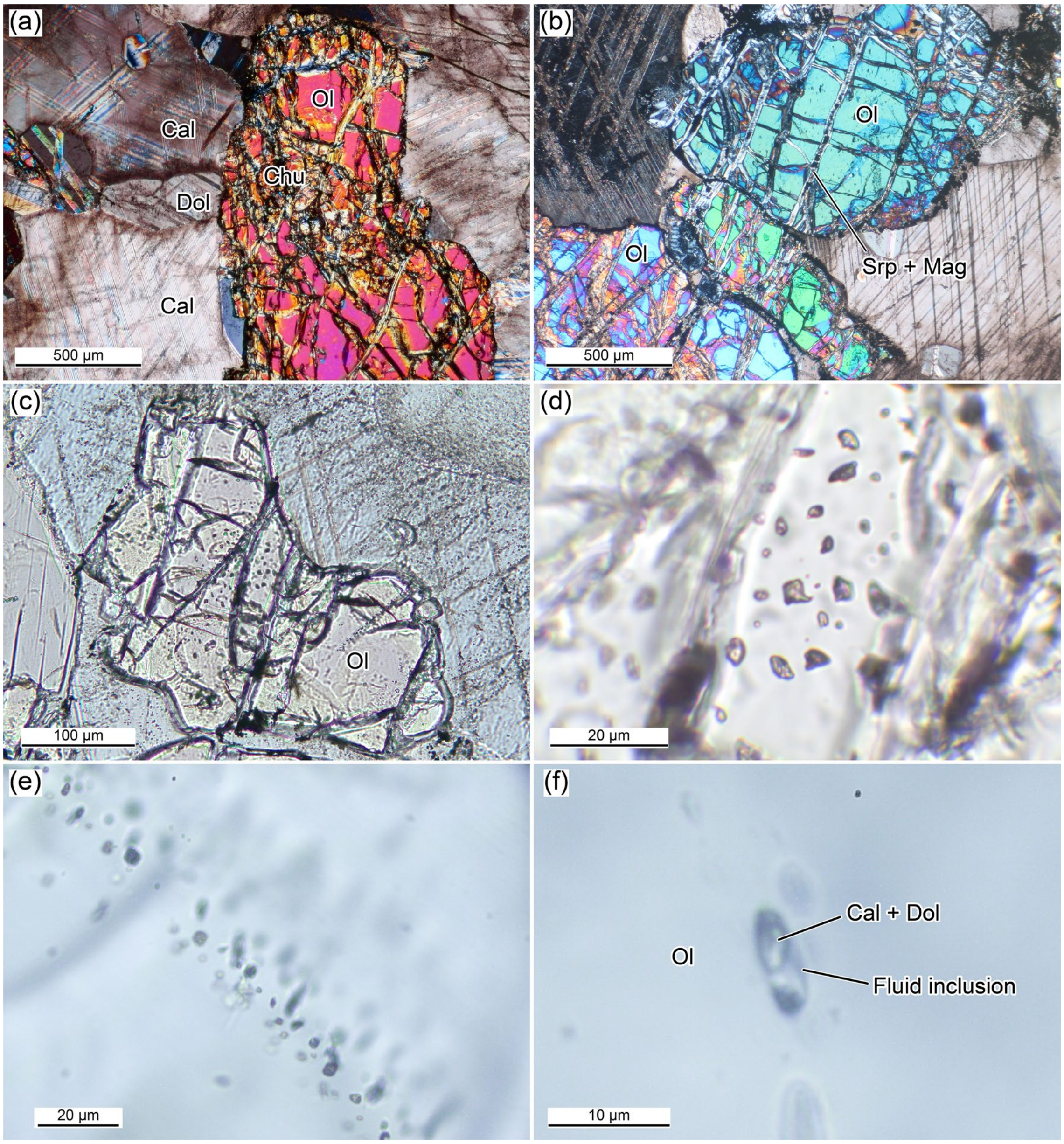

Fig. 2 Photomicrographs of investigated dolomitic marble. **a** Cross-polarized light (XPL) image of dolomitic marble. **b** XPL image of partially serpentinized olivine crystals in dolomitic marble. Serpentinization forms serpentine (lizardite) and magnetite. **c**, **d** Plane-polarized light (PPL) image of olivine crystals rich in fluid inclusions. **e** PPL image of olivine-hosted fluid inclusions with secondary nature. **f** PPL image of olivine-hosted primary fluid inclusion that contains calcite and dolomite. Mineral abbreviations follow Warr (2021)

grains were separated from sieved whole-rock powder using magnetic and heavy liquid techniques. Hand-picked olivine grains under a binocular microscope were mounted in 1-inch round epoxy resin discs. Olivine crystals in the investigated dolomitic marble often contain dark-colored fluid inclusions. The fluid inclusions vary from <1 to 10 µm in size and show irregular shape. There are two major types of olivine-hosted fluid inclusions, although discriminating between most inclusions is difficult. Primary fluid inclusions trapped during olivine growth occur as isolated inclusions, while secondary fluid inclusions, formed by fluid infiltration after olivine crystallization, occur as trails in olivine crystals (Fig. 2e). However, most inclusions are hard to discriminate as primary or secondary.

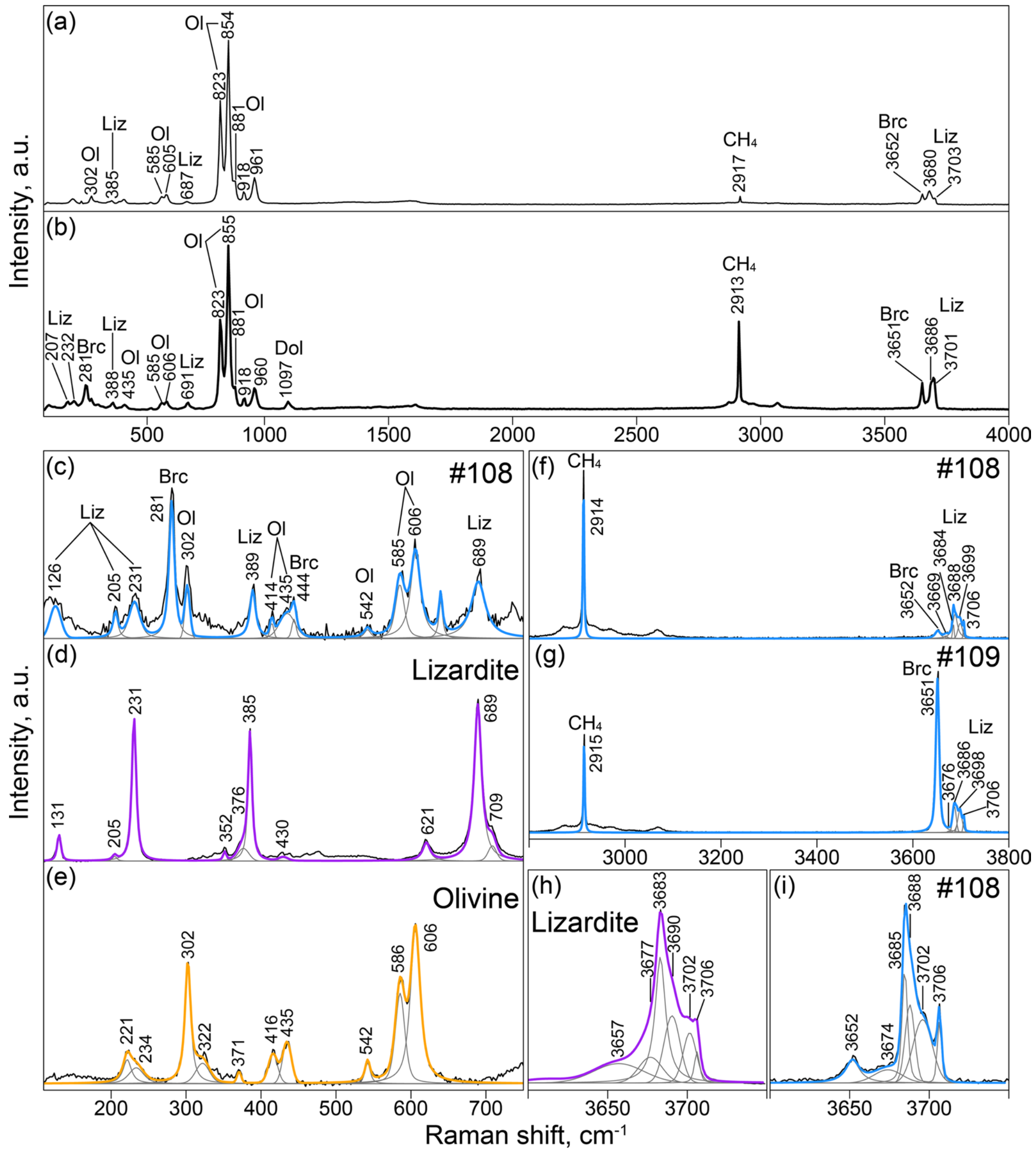

Fig. 3 Representative Raman spectra of olivine-hosted fluid inclusions in dolomitic marble from the Hida Belt. **a**, **b** Raman spectra of the olivine-hosted fluid inclusions. **c**–**e** Raman spectra of olivine-hosted fluid inclusion (**c**), lizardite in olivine rim (**d**), and host olivine (**e**) in low wavenumber spectral range (110–750 cm^{-1}). **f**, **g** Raman spectra of olivine-hosted fluid inclusion in high wavenumber spectral range (2800–3800 cm^{-1}). **h**, **i** Raman spectra of lizardite (**h**) and olivine-hosted fluid inclusion (**i**) in O–H stretching region (3600–3750 cm^{-1})

4.3 Raman spectroscopic analyses of olivine-hosted fluid inclusions

We performed Raman spectroscopic analyses for over 100 olivine-hosted fluid inclusions. Raman spectra of olivine-hosted fluid inclusions show a strong band at ~2913–2918 cm^{-1} (Figs. 3, 4, Additional file 1: Figure S1). This band can be assigned to the symmetric C–H stretching band of CH_4 vapor (e.g., Brunsgaard Hansen et al. 2001; Lu et al. 2007; Seitz et al. 1996). In addition to CH_4, several bands were observed in the high wavenumber region (~3600–3800 cm^{-1}) (Figs. 3,4, Additional file 1: Figure S1). These bands are originated from O–H stretching vibrations of hydrous minerals. On the low wavenumber region, Raman spectra of fluid inclusions show several bands in addition to the bands of the host olivine (Fig. 3c, e). The ~280 cm^{-1} and ~444 cm^{-1} bands (Fig. 3c) can be assigned to lattice vibrational modes of brucite (e.g., Dawson et al. 1973; Duffy et al. 1995; Zhu et al. 2019). Since brucite has a strong band at ~3650 cm^{-1} derived from O–H stretching vibration (e.g., Dawson et al. 1973; Duffy et al. 1995; Zhu et al. 2019), the ~3652 cm^{-1} band of

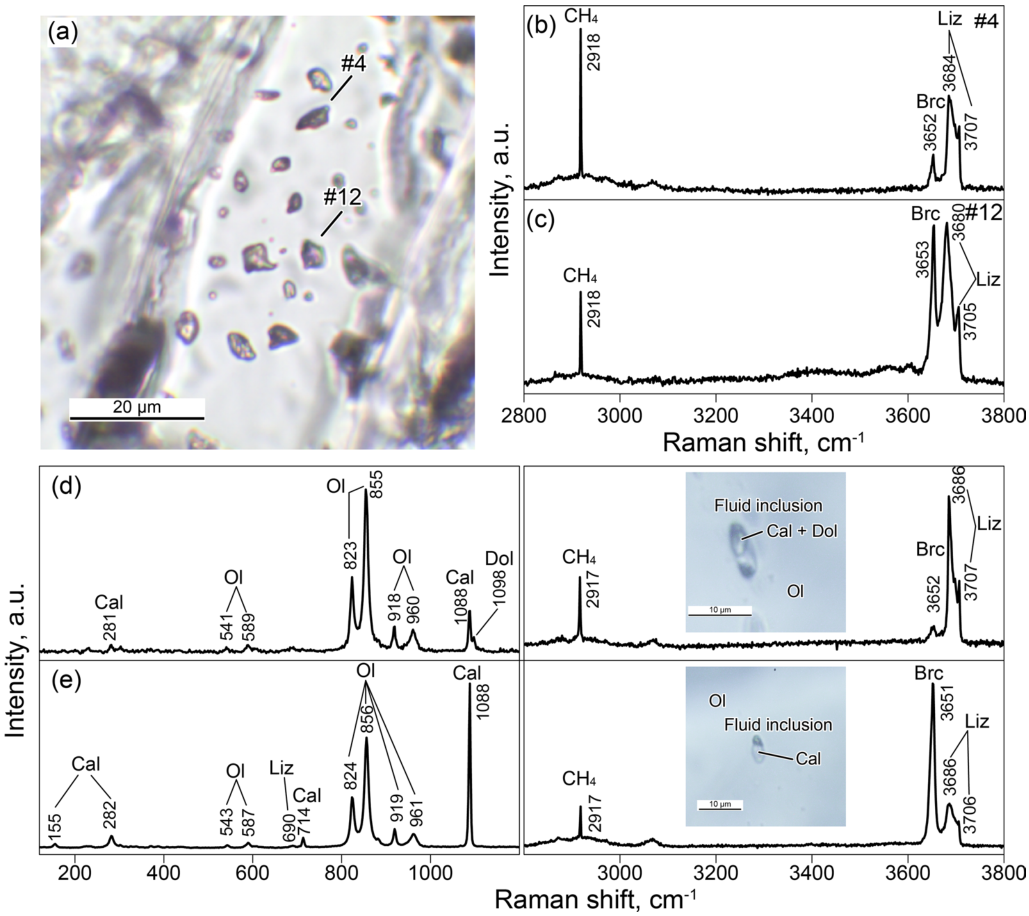

Fig. 4 Representative Raman spectra of olivine-hosted fluid inclusions. **a** PPL image of olivine-hosted fluid inclusions. **b**, **c** Raman spectra of the olivine-hosted fluid inclusions shown in (**b**). **d**, **e** Raman spectra of olivine-hosted fluid inclusions that contain carbonate minerals. Inclusion of **d** contains calcite and dolomite, and inclusions of **e** contains calcite

the fluid inclusion is attributed to brucite. In addition to olivine and brucite, Raman spectra of olivine-hosted fluid inclusions show ~130 cm^{-1}, 230 cm^{-1}, 390 cm^{-1}, and ~690 cm^{-1} bands (Fig. 3c). Similar peaks are also observed in matrix serpentine that occurs in rims and clacks of olivine crystals (Fig. 3d). We assigned these bands to serpentine minerals of lizardite or chrysotile (e.g., Auzende et al. 2004; Compagnoni et al. 2021; Groppo et al. 2006; Petriglieri et al. 2015; Rinaudo et al. 2003; Rooney et al. 2018; Tarling et al. 2018). Although lizardite and chrysotile have similar Raman spectra in the low wavenumber region, they can be distinguished by their O–H stretching bands in the high wavenumber spectral range (e.g., Auzende et al. 2004; Compagnoni et al. 2021; Petriglieri et al. 2015; Rooney et al. 2018; Tarling et al. 2018); lizardite has two major peaks while chrysotile has one peak with a slightly low wavenumber shoulder. Based on the presence of ~3685 cm^{-1} and ~3706 cm^{-1} peaks of the obtained spectrum (Fig. 3f, g, i), we considered that the serpentine in olivine-hosted fluid inclusions is lizardite. Raman spectrum of lizardite in high wavenumber spectral range consists of multiple bands (e.g., Auzende et al. 2004; Compagnoni et al. 2021). Compagnoni et al. (2021) obtained Raman spectra of lizardite under three different crystal orientations and deconvolved the O–H stretching region of lizardite into six bands. They reported that lizardite shows different Raman spectra and intensities for each orientation. Since we analyzed lizardite in fluid inclusions, it is difficult to perform a deconvolution that is completely consistent with the literature. Therefore, as previous studies have shown (Auzende et al. 2004; Petriglieri et al. 2015; Rooney et al. 2018; Tarling et al. 2018), we regarded that the Raman spectrum of lizardite in the O–H stretching region is characterized by two intense peaks at ~3680 cm^{-1} and >~3700 cm^{-1} (Fig. 3i). Although lizardite has a band of ~3650 cm^{-1}, it is not strong (Fig. 3h; Compagnoni et al. 2021; Rooney et al. 2018; Tarling et al. 2018). Hence, the intense peak

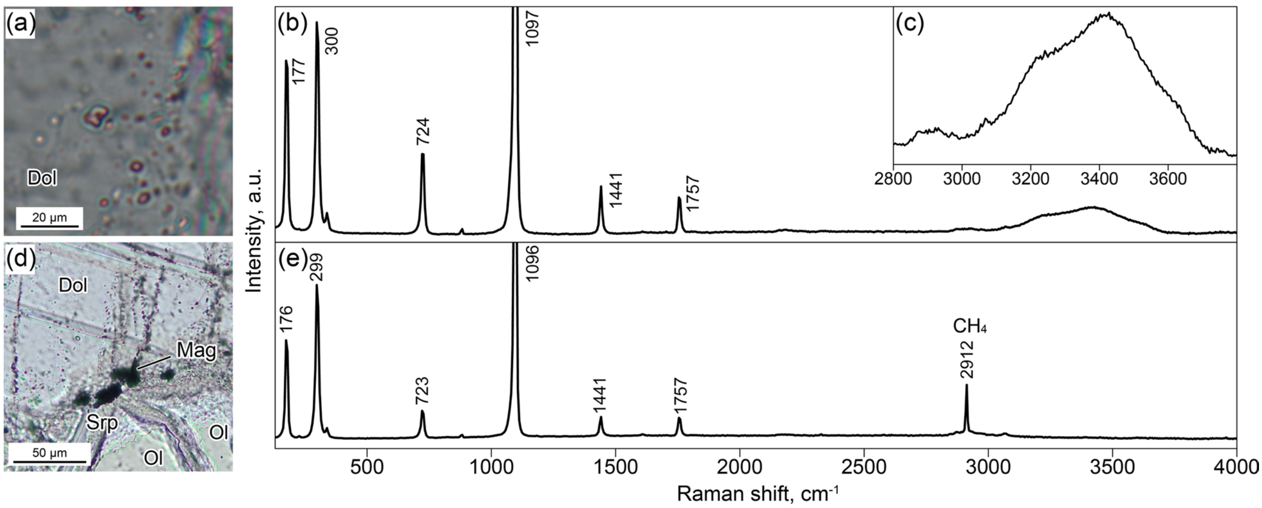

Fig. 5 Photomicrographs and representative Raman spectra of fluid inclusions in carbonate minerals. **a** PPL image of fluid inclusions in dolomite. **b** Raman spectrum of fluid inclusion in dolomite. Raman spectra of most fluid inclusions in calcite and dolomite show a broad band from around 2700–3800 cm^{-1}, which originates from O–H stretching modes of liquid water. **c** Enlarged view of O–H stretching region in the Raman spectrum of (**b**). PPL image (**d**) and Raman spectrum (**e**) of dolomite-hosted fluid inclusions that propagate from the serpentinized rim of olivine crystal

at ~3650 cm^{-1} can be considered to be that of brucite. Based on the above consideration, this study treats the Raman spectra of olivine-hosted fluid inclusions in the high wavenumber region as follows: The presence of brucite is characterized by the strong ~3650 cm^{-1} band, while other bands is derived from lizardite. Lizardite is characterized by two intense peaks at ~3680 cm^{-1} and >~3700 cm^{-1}. The CO_2, H_2O, and H_2 were not detected from investigated olivine-hosted fluid inclusions. The inclusion assemblage that contains CH_4, lizardite, and brucite was ubiquitously observed in investigated olivine-hosted fluid inclusions. In addition to the described inclusion assemblage, some primary fluid inclusions also contained carbonate minerals (Figs. 2f, 4d, e). Carbonate minerals in fluid inclusions show ~155 cm^{-1}, ~281 cm^{-1}, and ~714 cm^{-1} bands with a strong ~1088 cm^{-1} band (Fig. 4d, e) and are considered to be calcite. The peak position of the strong band of investigated carbonate mineral (~1088 cm^{-1}) was slightly higher than that of calcite in the literature (~1085 cm^{-1}: e.g., Bischoff et al. 1985; Dufresne et al. 2018; Gillet et al. 1993). The slight upshift of the band has been reported from Mg-calcite (e.g., Bischoff et al. 1985; Borromeo et al. 2017; Burke 2001), and the observed bands can be attributed to Mg-calcite. The ~1088 cm^{-1} band of Mg-calcite in fluid inclusions sometimes has a shoulder at a higher wavenumber side (~1098 cm^{-1}) (Fig. 4e), suggesting the presence of dolomite (e.g., Bischoff et al. 1985; Gillet et al. 1993). Since calcite and dolomite also occur as inclusion minerals in the olivine, carbonate minerals in fluid inclusions are considered an accidentally trapped mineral during host olivine growth.

4.4 Fluid inclusions in carbonate minerals

Calcite and dolomite also contained fluid inclusions (Fig. 5a, d). Raman spectra of most fluid inclusions in calcite and dolomite show a broad band from around 2700–3800 cm^{-1} (Fig. 5b, c), which is attributed to O–H stretching modes of liquid water (e.g., Walrafen 1964). Secondary fluid inclusions that propagate from the serpentinized rim of olivine crystals were rare and contained CH_4 (Fig. 5d, e). Note that these secondary CH_4 fluid inclusions in carbonate minerals lack H_2O.

5 Discussion

5.1 Origin of CH_4-bearing olivine-hosted fluid inclusions

Raman spectroscopic analysis of olivine-hosted fluid inclusions in dolomitic marble found the presence of CH_4, lizardite, and brucite (Figs. 3, 4, Additional file 1: Figure S1). The presence of serpentine and brucite in fluid inclusions is robust evidence that serpentinization occurred within olivine-hosted fluid inclusions as the result of the reaction between trapped fluid and host olivine crystals (Fig. 6). Therefore, it is reasonable to consider that the CH_4 was produced via the reduction of CO_2 by H_2 that originated from internal serpentinization within fluid inclusions (Grozeva et al. 2020; Klein et al. 2019; Miura et al. 2011; Zhang et al. 2021, 2022).

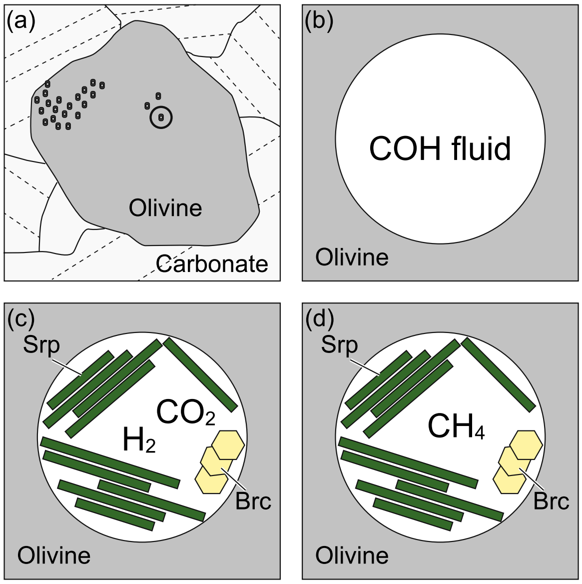

Fig. 6 Schematic diagram illustrating a model of serpentinization and accompanying CH_4 generation within olivine-hosted fluid inclusions. **a** Petrography of olivine-bearing dolomitic marble. **b** Olivine-hosted fluid inclusions originally contained H_2O and CO_2 (COH fluid) when they were trapped. **c** The decrease in temperature during the early stages of exhumation causes serpentinization of host olivine by trapped fluid and H_2 generation. **d** Generated H_2 reduced CO_2 and formed CH_4

Based on the observation, we postulate that olivine-hosted fluid inclusions originally contained H_2O and CO_2 (COH fluid) when they were trapped. As temperatures decreased upon exhumation, the trapped fluid caused serpentinization of the host olivine crystal and formed lizardite and brucite as step-daughter minerals. The serpentinization reaction generated H_2, and then the H_2 reduced CO_2 and formed CH_4. The origin of CO_2 in the trapped fluid can be attributed to metamorphic decarbonation and/or carbonate dissolution. The entrapment of primary fluid inclusions occurred during olivine growth in the upper-amphibolite to granulite facies peak metamorphic conditions of the Hida Belt. Since the formation of serpentine in fluid inclusions occurred after the fluid entrapment, the secondary fluid inclusions must have been trapped at conditions under which olivine is stable in the presence of H_2O. In other words, the fluid entrapment occurred prior to the matrix serpentinization of the host olivine crystal. Therefore, we can rule out the possibility that the CH_4 was derived from matrix serpentinization and was present in the fluid when it was trapped.

Although typical serpentinization reactions accompany the oxidation of iron and form magnetite, resulting in H_2 generation, the mineral inclusion assemblage of investigated olivine crystals lacks magnetite (Figs. 3, 4). However, there is a possibility that nanometer-sized magnetite crystals that cannot be detected by Raman spectroscopic analyses may be present in inclusions. Even if not, magnetite formation is not essential in H_2 production during serpentinization. Serpentine can accommodate a significant amount of ferric iron (Fe^{3+}) (e.g., Andreani et al. 2013; Fuchs et al. 1998; Klein et al. 2009; O'Hanley and Dyar 1993). Serpentine produced by the hydration of magnesium (Mg)-rich olivine contains Fe with a high $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio (Klein et al. 2013). The mineral assemblage formed by serpentinization depends on conditions such as temperature and water to rock ratio; magnetite may not be produced by the serpentinization of Fe-bearing olivine (Klein et al. 2013). In that case, the Fe^{3+} in serpentine contributes to the H_2 generation (e.g., Andreani et al. 2013; Klein et al. 2013; Marcaillou et al. 2011; Seyfried et al. 2007). Therefore, the absence of magnetite does not exclude the possibility of H_2-generation via serpentinization within fluid inclusions.

Secondary fluid inclusions in carbonate minerals that propagate from serpentine contained CH_4 and lacked H_2O. In contrast, the ubiquitous occurrence of hydrous minerals like serpentine and brucite in olivine-hosted fluid inclusions indicates that the inclusions initially contained H_2O. The contrast regarding the presence of water in fluid inclusions in olivine and carbonate minerals may reflect differences in the original fluid composition. Since CH_4 secondary fluid inclusions in calcite and dolomite propagate from serpentine, the origin of CH_4 in carbonate minerals can be attributed to the matrix serpentinization of olivine crystals, which formed serpentine minerals of olivine rim and clacks. Therefore, the entrapment timing of CH_4-bearing fluid inclusions hosted in olivine and carbonate minerals would have been different: Olivine-hosted fluid inclusions were trapped prior to the matrix serpentinization, whereas CH_4 secondary fluid inclusions in calcite and dolomite were formed during or after the serpentinization. Raman spectra of most of the fluid inclusions in calcite and dolomite show the presence of liquid H_2O. If these inclusions were formed during regional metamorphism, metamorphic fluid would not have contained CH_4. Fluid inclusions in carbonate minerals may support the abiotic CH_4 generation within olivine-hosted fluid inclusions. The possibility that the CH_4 in olivine-hosted fluid inclusions is of biological origin cannot be completely ruled out without measuring the carbon isotope compositions of the CH_4. However, the presence of H_2O-rich fluid inclusions in carbonate minerals and the mineralogy of olivine-hosted fluid inclusions indicate that the abiotic synthesis during internal serpentinization within fluid inclusions is a plausible origin of CH_4 in olivine-hosted fluid inclusions of dolomitic marble.

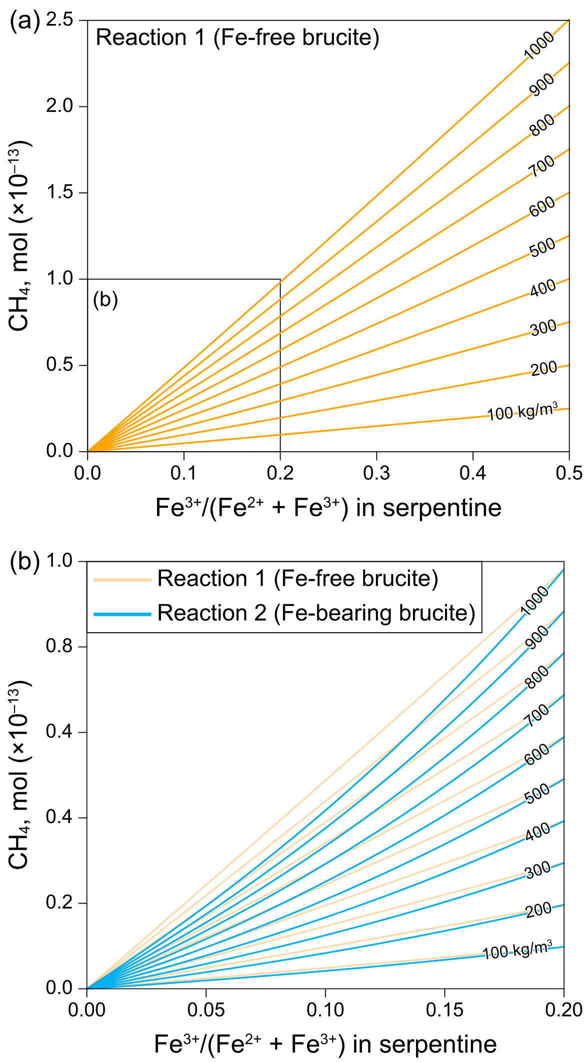

Fig. 7 The estimation of the amount of CH_4 produced within olivine-hosted fluid inclusions. Assuming spherical fluid inclusions with a diameter of 10 μm, the amount of CH_4 that could be produced by serpentinization without magnetite formation is calculated. The results of two simple reactions are shown; produced brucite is **a** Fe-free brucite and **b** Fe-bearing brucite. The number on the lines shows the assumed density of H_2O (100–1000 kg/m^3)

Assuming spherical fluid inclusions with a diameter of 10 μm, we estimated the amount of CH_4 that could be produced by the serpentinization without magnetite formation as a function of Fe^{3+} content in serpentine (Fig. 7). Two simple reactions were considered, one in which the product brucite is a pure Mg end-member (Reaction 1) and one in which the product brucite contains Fe (Reaction 2).

$$\begin{aligned} & a\left(\mathrm{Mg}_{0.9},\mathrm{Fe}_{0.1}\right)_2\mathrm{SiO}_4 + b\mathrm{H}_2\mathrm{O} \quad (\text{Olivine}) \\ & \rightarrow c\left(\mathrm{Mg}_x,\mathrm{Fe}^{2+}_y,\mathrm{Fe}^{3+}_z\right)\left(\mathrm{Fe}^{3+}_v,\mathrm{Si}_w\right)_2\mathrm{O}_5(\mathrm{OH})_4 \quad (\text{Serpentine}) \\ & + d\mathrm{Mg(OH)}_2 \quad (\text{Brucite}) + e\mathrm{H}_2. \end{aligned} \tag{1}$$

$$\begin{aligned} & a\left(\mathrm{Mg}_{0.9},\mathrm{Fe}_{0.1}\right)_2\mathrm{SiO}_4 + b\mathrm{H}_2\mathrm{O} \quad (\text{Olivine}) \\ & \rightarrow c\left(\mathrm{Mg}_x,\mathrm{Fe}^{2+}_y,\mathrm{Fe}^{3+}_z\right)\left(\mathrm{Fe}^{3+}_v,\mathrm{Si}_w\right)_2\mathrm{O}_5(\mathrm{OH})_4 \quad (\text{Serpentine}) \\ & + d\left(\mathrm{Mg}_s,\mathrm{Fe}_t\right)(\mathrm{OH})_2 \quad (\text{Brucite}) + e\mathrm{H}_2. \end{aligned} \tag{2}$$

For simplicity, the following assumptions were made. (1) Generated H_2 is not lost by diffusion. (2) Trapped fluid initially contains H_2O and CO_2, and the amount of CO_2 is sufficient to react with the generated H_2. (3) Among the products, only serpentine contains Fe^{3+}. Since we regard cronstedtite [$(Fe^{2+}{}_2Fe^{3+})_3(Fe^{3+}Si)_2O_5(OH)_4$] as the Fe^{3+} end-member of serpentine (Evans 2008), the Fe^{3+}/(Fe^{2+} + Fe^{3+}) ratio of serpentine is up to 0.5. The serpentine formed by the serpentinization of Fo_{90} olivine has a Fe^{3+}/(Fe^{2+} + Fe^{3+}) ratio up to ~0.35 (Klein et al. 2013). Assuming the density of trapped H_2O is 1000 kg/m^3, each fluid inclusion has the potential to produce a maximum of ~1.7×10^{-13} mol CH_4. This CH_4 amount is comparable to the CH_4 content of olivine-hosted fluid inclusions in peridotite and gabbroic rocks (8.4×10^{-14} to 1.2×10^{-11} mol CH_4: Klein et al. 2019). Although the actual serpentinization reaction would be more complex, and this is a maximum estimation, it suggests the effective production of CH_4 in olivine-hosted fluid inclusions in dolomitic marble.

5.2 Implications for abiotic CH_4 synthesis during serpentinization

What is the significance of CH_4 synthesis in olivine-hosted fluid inclusions? Thermodynamic calculations show that serpentinization involving a small volume of fluid results in high H_2 concentration in fluids because the generated H_2 is less diluted (Klein et al. 2013). Olivine-hosted fluid inclusions can achieve a high H_2 concentration during serpentinization because the volume of trapped fluid is much smaller than the volume of the host olivine crystal. In addition, the infiltration of external fluids would not occur during serpentinization due to the isolated nature of the fluid inclusions within the olivine. This condition would be suitable for the reduction of CO_2 and production of CH_4. Experimental studies suggest that there are substantial kinetic barriers inhibiting abiotic CH_4 synthesis from the reduction of CO_2 unless certain catalysts, such as

FeNi alloys and chromite, are present (e.g., Foustoukos and Seyfried 2004; Horita and Berndt 1999; Klein and McCollom 2013; Lazar et al. 2012; McCollom 2016; McCollom and Seewald 2001); longer reaction times may be necessary to produce a significant amount of abiotic CH_4. However, fluid inclusions can retain high H_2 concentrations over much longer timescales than experimental studies. Therefore, internal serpentinization within fluid inclusions can be an effective pathway of abiotic CH_4 synthesis in the geological process.

High concentrations of geologically sourced hydrogen and hydrocarbon can have an impact on the Earth's biological activities. The microbial habitat extends to beneath Earth's surface, and Earth's subsurface biosphere, which has a large biomass (Magnabosco et al. 2018), relies for metabolisms on H_2 and CH_4 produced by fluid-rock interactions (e.g., Colman et al. 2017; Templeton and Caro 2023). In fact, some subsurface microbial communities would use serpentinite-derived H_2 and CH_4 (e.g., Schrenk et al. 2013). Recently, Vitale Brovarone et al. (2020) found that serpentinization generates reduced fluids, including H_2, CH_4, H_2S, and NH_3, and they suggested that these fluids may supply to the subsurface biosphere in the forearc region. In this study, we proposed the abiotic CH_4 synthesis in olivine-hosted fluid inclusions of dolomitic marble. The presence of microorganisms with anaerobic methane oxidation has been reported from granitic rocks as well as basalts and serpentinites (e.g., Ino et al. 2016; Kraus et al. 2021; Lever et al. 2013; Nothaft et al. 2021). If the olivine-hosted fluid is released, dolomitic marble may have the potential to provide abiotic CH_4 to the subsurface biosphere in the continental crust.

Abiotic CH_4 synthesis through internal serpentinization within olivine-hosted fluid inclusions has been widely recognized in mafic and ultramafic rocks (Grozeva et al. 2020; Klein et al. 2019; Miura et al. 2011; Zhang et al. 2021, 2022). This study provides the first finding of CH_4-bearing olivine-hosted fluid inclusions in metacarbonate rocks with sedimentary origin. We propose that serpentinization within olivine-hosted fluid inclusions is a ubiquitous process in olivine-bearing lithologies, not only in ultramafic rocks. Furthermore, since olivine-bearing dolomitic marbles occur in various orogenic belts with a wide range of metamorphic conditions (e.g., Kato et al. 1997; Liu et al. 2006; Ogasawara et al. 2000; Otsuji et al. 2013; Satish-Kumar et al. 2010; Yoshida et al. 2021), and even in contact metamorphic aureoles (e.g., Cook and Bowman 2000; Ferry et al. 2002; Holness 1997; Rice 1977), the dolomitic marble might have the potential to be the key lithology for the synthesis and storage of abiotic CH_4 in the continental crust and orogenic belts. In addition, the CH_4 in olivine-hosted fluid inclusions can be released by the weathering of exhumed dolomitic marble, and it might affect the atmospheric CH_4. To further our understanding of the contributions to the impact of abiotic CH_4 storage in the solid Earth, quantitative estimation of CH_4 production is still required.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40645-024-00609-y.

Additional file 1: Figure S1. Representative Raman spectra of olivine-hosted fluid inclusions in high wavenumber spectral range (2800–3800 cm^{-1}).

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Author contributions
HH devised the project, conducted the analysis, and drafted the manuscript. TT supervised the project and contributed to the writing of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analyzed during this study are included in this published article.

Declarations

Competing interests
The authors declare that they have no competing interest.

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