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This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Peng, W.G., Tumiati, S., Zhang, L.F., Tiraboschi, C., Vitale Brovarone, A., Toffolo, L., et al. (2022). An Experimental Study on Kinetics-Controlled Ca-Carbonate Aqueous Reduction into CH4 (1 and 2 GPa, 550 degrees C): Implications for C Mobility in Subduction Zones. JOURNAL OF PETROLOGY, 63(8), 1-18 [10.1093/petrology/egac070].

Availability:

This version is available at: https://hdl.handle.net/11585/903836 since: 2023-06-13

Published:

DOI: http://doi.org/10.1093/petrology/egac070

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JOURNAL OF PETROLOGY VOL. 63 ISSN 0022-3530

DOI: 10.1093/petrology/egac070

The final published version is available online at: <u>https://dx.doi.org/10.1093/petrology/egac070</u>

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An experimental study on kinetics-controlled Ca-carbonate aqueous reduction into CH₄ (1 and 2 GPa, 550 °C): Implications for C mobility in subduction zones

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Running Title: Abiotic CH₄ generation in subduction zones

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ABSTRACT

Abiotic methane (CH₄) generation under subduction zone conditions has been experimentally investigated through aqueous reduction of pure C-bearing materials (e.g. carbonate minerals and organic matter). However, quantitative assessments of CH₄ production in these experiments, as well as the potential effects of other components such as silica (Si) on the reduction processes, have not yet been well established. Here, we performed experiments to quantitatively evaluate the timeresolved Ca-carbonate aqueous reduction into CH_4 at P = 1 and 2 GPa, and T = 550 $^{\circ}$ C in the CaO + COH, CaO + SiO₂ + COH, and CaO + SiO₂ + MgO + COH systems, employing calcite + water \pm quartz \pm serpentine (synthetic chlorine (Cl)bearing chrysotile and natural Fe-Al-bearing antigorite) as starting materials. Redox conditions of the experiments were buffered by iron-wüstite (IW) using a double capsule setting, corresponding to oxygen fugacity (fO_2) values (expressed as log units relative to the fayalite-magnetite-quartz buffer, ΔFMQ) in the inner capsule of $\Delta FMQ \approx -5.5$ at 1 GPa and $\Delta FMQ \approx -6.0$ at 2 GPa. The solid products are mainly composed of portlandite \pm larnite \pm wollastonite \pm brucite, while Cacarbonate and/or silicate reactants commonly occur as relicts. Quadrupole mass spectrometric analysis shows that CH_4 and H_2O are the major COH molecular species in the fluid products, with molar ratios between CH₄ and starting calcite representing the reaction progress ranging from ~0.13 to ~1.00. Comparisons of

experimental run products with thermodynamically predicted phase assemblages, together with time-series experiments, indicate that the reduction processes are primarily controlled by reaction kinetics. At 1 GPa and 550 °C, rate constants of 4.0 $\times 10^{-6}$ s⁻¹, 7.4 $\times 10^{-6}$ s⁻¹, and 2.6 $\times 10^{-6}$ s⁻¹ were retrieved for reactions starting with calcite + quartz + water, calcite + synthetic Cl-bearing chrysotile + water, and calcite + natural Fe-Al-bearing antigorite + water, respectively, significantly higher than the constant of 0.8×10^{-6} s⁻¹ for the silicate-absent reaction. Besides, an increase in pressures can also enhance the reduction efficiency of Ca-carbonates until reaching equilibrium with the fluids. Our data provide experimental evidence for kinetics-controlled Ca-carbonate aqueous reduction into CH₄ in subduction zones, indicating that silicate involvement and/or pressure increase can accelerate the reaction rates through short-lived fluid-rock interactions, which may have important implications for deep C mobility.

Key words: abiotic CH₄; Ca-carbonate aqueous reduction; deep C mobility; experimental petrology; reaction kinetics

INTRODUCTION

Investigating the geological production of CH_4 may be essential for deciphering the chemolithoautotrophic origin of life on Earth and other planetary bodies in our

solar system (e.g. Kelley et al., 2005; Russell et al., 2010; McCollom & Seewald, 2013; Plümper et al., 2017; Klein et al., 2019; Ménez, 2020; Truche et al., 2020; Vitale Brovarone *et al.*, 2020). The generation of CH_4 on Earth can be attributed to either biotic or abiotic processes. Biotic CH₄ is widely distributed in surface environments, originating primarily from microbial processes or thermogenic degradation of organic matter. Abiotic CH₄, formed by chemical reactions that are independent from biotic processes, has been recognized over a wide range of geological contexts particularly in submarine serpentinite-hosted hydrothermal fields and Precambrian crystalline shields (see Etiope & Sherwood Lollar, 2013 and Etiope & Schoell, 2014 for reviews). Furthermore, an increasing number of field and experimental studies have been conducted on abiotic CH₄ generation under subduction zone conditions, offering potential insights into the mechanisms of deep C mobility (Scott et al., 2004; Shi et al., 2005; Sachan et al., 2007; Sharma et al., 2009; Song et al., 2009; Arai et al., 2012; Lazar et al., 2014; Huang et al., 2017; Li, 2017; Mukhina et al., 2017; Vitale Brovarone et al., 2017, 2020; Tao et al., 2018; Giuntoli et al., 2020; Boutier et al., 2021; Peña-Alvarez et al., 2021; Peng et al., 2021; Zhang et al., 2021; Spránitz et al., 2022).

Redox states in subduction zones, described using variables like fO_2 , μO_2 (O_2 chemical potential), or nO_2 (O_2 molar quantity) (Tumiati *et al.*, 2015), modulate the valence and speciation of subducted C such as carbonate minerals, CO₂,

graphite/diamond, and CH₄ (e.g. Hayes & Waldbauer, 2006; Evans, 2012; Galvez & Pubellier, 2019; Tumiati & Malaspina, 2019; Sheik et al., 2020). At relatively oxidized conditions where C^{4+} is stable, interactions between COH fluids and several slab- and mantle wedge-derived lithologies at forearc to subarc depths commonly generate carbonate minerals, contributing to C sequestration in subduction zones (e.g. Tumiati et al., 2013; Piccoli et al., 2016, 2018, 2021; Scambelluri et al., 2016; Jaeckel et al., 2018; Sieber et al., 2018, 2020, 2022; Consuma et al., 2020; Peng et al., 2020; Hu et al., 2021; Okamoto et al., 2021). Conversely, reduced C including hydrocarbons (e.g. CH₄) and graphite would progressively become dominant C-bearing species imposed by decreasing fO_2 at convergent margins, as suggested by both rock-based investigations and experimental simulations (see below). Subduction-related production of CH₄ has been recorded in ophicalcites from the Italian Western Alps, ascribed to calcite methanation induced by H₂-riched fluids at Δ FMQ -6.0 to -3.0 at 1.0-2.0 GPa and 400-500 °C (Vitale Brovarone et al., 2017; Giuntoli et al., 2020). Besides, CH₄bearing fluid inclusions were reported in carbonated eclogites from the Chinese southwestern Tianshan, which, combined with experimental studies, demonstrates aqueous reduction of Fe-bearing dolomite at Δ FMQ -2.5 to -1.5 at 2.5-3.0 GPa and 500-575 °C (Tao et al., 2018). Further, abiotic CH₄ generation in exhumed ophidolomites from the Chinese southwestern Tianshan has underscored the

potential role of hydrogen fugacity (fH_2) in carbonate reduction in subduction zones, elucidating that an infiltration of H₂O-rich fluids characterized by relatively high fH_2 can result in dolomite transformation into CH₄ starting at 0.7–0.9 GPa and 410–430 °C (Peng et al., 2021). In addition to carbonate-bearing lithologies, abiotic CH₄ has also been observed in several slab- and mantle wedge-derived partially serpentinized rocks, as well as orogenic peridotites, interpreted as resulting from reduction of C-bearing species in metamorphic fluids through subduction zone serpentinization (Sachan et al., 2007; Vitale Brovarone et al., 2020; Boutier et al., 2021; Zhang et al., 2021). Experiments conducted at 1.5–2.5 GPa and 600–700 °C (Li, 2017) and 2.4–3.5 GPa and 300 °C (Huang) et al., 2017) suggest that aqueous reduction of carboxylic acids or carboxylates represents a potential pathway leading to the formation of CH₄ (commonly with other short-chain hydrocarbons) in subduction zones. Moreover, several experiments have evaluated the important role of low fO_2 far below the FMQ buffer in high-pressure (HP) Ca-carbonate aqueous reduction into CH₄ (see below). Experiments performed by Lazar et al. (2014) in the CaO + COH system at 0.2–1.0 GPa and 300–700 $^{\circ}$ C indicate that low values buffered by iron-magnetite (IM) or wüstite-magnetite (WM) are fOa favorable for the reduction of subducted calcite into CH₄. Similar conclusions were reached by Mukhina et al. (2017) who observed high yields of hydrocarbons (mostly CH_4) in the CaO + Fe/FeO + COH system buffered by iron or IW at

2.0–6.6 GPa and 400–600 °C. The reported experiments mainly qualitatively evaluated the effects of $P-T-fO_2$ conditions on abiotic CH₄ generation through aqueous reduction of pure C-bearing materials. However, little attention has been paid to the quantification of CH₄ in such reduction experiments that are dependent on run durations (Barbier *et al.*, 2020 and references therein). Experiments have suggested that the dissolved SiO₂ in subduction zone aqueous fluids may induce partial dissolution of graphite by synthesizing organic complexes, thereby contributing to elevated CO₂ concentrations in the fluids (Tumiati *et al.*, 2017, 2020). Nevertheless, it remains undetermined whether SiO₂, a key component comprising lithospheric rocks mainly in the form of silicates, can influence Cacarbonate aqueous reduction and thus CH₄ production under subduction zone conditions.

In this contribution, we experimentally investigated kinetics-controlled abiotic CH_4 formation through Ca-carbonate aqueous reduction in the CaO + COH, CaO + $SiO_2 + COH$, and CaO + $SiO_2 + MgO + COH$ systems buffered by IW both at 1 and 2 GPa at 550 °C (24–264 h), using calcite + water ± quartz ± serpentine (synthetic Cl-bearing chrysotile (hereafter referred to as synthetic chrysotile) and natural Fe–Al-bearing antigorite (hereafter referred to as natural antigorite)) as starting materials. Experimental and modelling results of solid and fluid products, as well as calculations for reaction rates, are shown and discussed to improve our

comprehension of the kinetics-controlled reduction processes in subduction zones. For comparison, dry and/or wet experiments starting with calcite, quartz, synthetic chrysotile, and natural antigorite separately were performed under the same $P-T-fO_2$ conditions, to investigate whether CH₄ can be produced by dry reduction of Ca-carbonates and to evaluate whether the silicate reactants were hosts for Cbearing materials representing the potential contaminants. Chemical formulas and abbreviations of phases in this study are listed in Table 1.

EXPERIMENTAL METHODS

Experimental conditions and apparatus

Experiments were performed with an end-loaded piston-cylinder apparatus at P = 1and 2 GPa, and T = 550 °C in the Experimental Petrology Laboratory of the Department of Earth Sciences, University of Milan (Italy). Pressure calibration of the piston-cylinder apparatus is based on the quartz–coesite transition (Bose & Ganguly, 1995) at 2.93 GPa and 800 °C, and 3.07 GPa and 1000 °C, resulting in an accuracy of \pm 0.01 GPa. Temperatures were measured using a K-type thermocouple with an accuracy of \pm 5 °C. Samples were first pressurized at the run pressures and then heated to 550 °C, with a ramp of ~100 °C/min. Experiments were quenched by turning off the power supply, leading to a high rate of temperature decrease of > 40 °C/s, and thus compositions of the quenched COH fluids as well as solid phases (see below) are considered to represent those at the experimental P-T conditions (e.g. Matveev *et al.*, 1997; Tiraboschi *et al.*, 2022). After quenching, capsules (see below) were recovered and cleaned with hydrochloric acid. The outer capsule was peeled off, exposing the inner capsule, and dried in a vacuum oven at 110 °C (> 2 h) to eliminate the residual water trapped in the oxygen buffer (Tiraboschi *et al.*, 2016; Tumiati *et al.*, 2020).

Starting materials and buffering strategy

The conventional double capsule technique (Eugster & Skippen, 1967) was employed to constrain fH_2 conditions (and, indirectly, redox states) of the experiments and to prevent the direct contact of starting materials with the IW buffer. Starting materials were loaded in an inner Au₆₀Pd₄₀ capsule (OD = 2.3 mm), which was placed in an outer Au capsule (OD = 4.5 mm) containing the buffering assemblage. Reagent-grade pure calcite powder (Sigma-Aldrich), natural hyaline quartz powder, synthetic chrysotile containing ~1 wt% Cl (provided by Marcello Campione, University of Milan-Bicocca; Villa *et al.*, 2018), natural antigorite containing ~4 wt% FeO and ~2 wt% Al₂O₃ from the Western Alps (provided by Chiara Groppo, University of Turin; Vitale Brovarone *et al.*, 2017), and ultrapure Milli-Q water were used as starting materials. In experiments starting with a single kind of mineral with or without added water, the solid reactant (calcite, quartz, synthetic chrysotile, or natural antigorite) was evenly distributed in the inner capsule (e.g. calcite + water in Fig. 1a). By contrast, in experiments starting with calcite and another mineral (quartz, synthetic chrysotile, or natural antigorite) with added water, solid reactants were layered in the inner capsule (Fig. 1b and c). relatively short run durations in this study, the layered starting materials allowed the preservation of chemical gradients in the inner capsule, so that the fluid products could coexist with a variety of solid phases, even if metastable, to investigate their effects on the kinetics of Ca-carbonate aqueous reduction into CH₄ (see Section Discussion). The double capsule was embedded in a sintered MgO rod (Norton Ceramics), surrounded by a graphite heater and a NaCl sleeve. A pyrophyllite-steel plug was placed at the top of the assembly to ensure electrical contact. Since the Au₆₀Pd₄₀ allow of the inner capsule is permeable to H₂, fH₂ conditions in the inner capsule are expected to be the same as those in the outer capsule (Tiraboschi et al., 2016, 2018; Tumiati et al., 2017, 2020). The starting IM buffer (with added excess water) has always been converted into the IW buffer during experimental runs (Fig. 1d), which remains stable at the studied P-Tconditions (Fig. 1e; e.g. Eugster & Wones, 1962; Jenkins & Bozhilov, 2003). Thus, the IW buffer constrained fH_2 values in both inner and outer capsules by the following reaction throughout the runs, as reflected by the preservation of all the buffering phases after quenching (Fig. 1d):

$$Fe + H_2O \rightleftharpoons FeO + H_2.$$
 (1)

Since fO_2 conditions in the inner and outer capsules are identical only when both of them contain pure water (Eugster & Skippen, 1967), fO_2 values in the inner capsule are expected to be slightly lower than fO_2^{IW} (Luth, 1989; Tumiati *et al.*, 2017, 2020; Miozzi & Tumiati, 2020) in our experiments where fluids are nearly binary mixtures of CH₄ and H₂O (Table 2).

ANALYTICAL TECHNIQUES

Analysis of solids

Chemical analysis, back-scattered electron imaging, and element mapping of the solid products were conducted using a JEOL 8200 wavelength-dispersive electron microprobe at the Department of Earth Sciences, University of Milan (Italy). The running conditions were 15 kV acceleration voltage and 5 nA beam current, with a beam diameter of ~1 µm. The adopted mineral standards were grossular (Si, Al, and Ca), ilmenite (Ti), pure Cr (Cr), fayalite (Fe), rhodonite (Mn), olivine (Mg), and orthoclase (K). A counting time of 30 s (10 s background) was applied for all the elements. The PRZ correction was performed at the final calibration stage.

Analysis of fluid species

To measure COH molecular species in the fluid products, we employed the capsule-piercing technique (Tiraboschi et al., 2016; see also Tiraboschi et al., 2022 for a review with respect to the quantification of COH fluids through ex situ experiments) at the Department of Earth Sciences, University of Milan (Italy) After quenching, fluids were extracted from the inner capsule in a Teflon extraction vessel (reactor), which was heated by an electric furnace to ~90 °C to convert liquid water into water vapor. Then, fluids were conveyed into a quadrupole mass spectrometer (QMS) using ultrapure argon (Ar) as the carrier gas. The QMS was connected to the reactor by a heated line $(\sim 90 \degree C)$ to avoid water vapor condensation on metal tubes. Pressures in the reactor were measured by a highresolution sensor gauge, with an accuracy of ± 1 mbar. Temperatures in the reactor were monitored by a K-type thermocouple. The internal volume of the reactor was constrained based on the distance between its base and top parts. Thus, the total moles of gases (n) released from the inner capsule were retrieved using the ideal gas law $n = \Delta P^* V (R^*T)$, where ΔP is the pressure increase in the reactor after piercing, V is the volume of the reactor, R is the gas content, and T is the temperature in the reactor during piercing.

During the QMS analysis, selected mass/charge (m/z) channels were monitored to measure the COH fluid species. The QMS calibration was performed using double-distilled water (typically 1 µL) and three gas mixtures with known compositions (80 vol% Ar + 10 vol% CO₂ + 10 vol% O₂, 80 vol% Ar + 10 vol% $CH_4 + 10$ vol% CO, and 90 vol% Ar + 10 vol% H₂). The calibration enables the retrieval of micromoles (µmol) of H2O, CH4, CO2, CO, H2, and O2, with uncertainties of ~1 mol% for all the species except for CO (~10 mol%) due to the interference of atmospheric N₂ on the 28 m/z channel (Tumiati *et al.*, 2020). When the fluid products were transferred into the QMS, micromolar concentrations of COH molecular species were obtained by comparing the integrated fragmentation peaks of characteristic m/z channels (e.g. channels 15, 14, 12, and 2 for CH₄; see Supplementary Data Fig. S1 for a representative channel 15 in runs COH115 and COH116) with those of the calibration gases, taking into account all possible interferences using a least squares regression method (Tiraboschi et al., 2016). Monte Carlo simulations provided the propagation of uncertainties for the COH fluid species, corresponding to their measurement uncertainties. Further, the measured concentrations of COH molecular species, as well as their uncertainties, were recalculated based on the total amounts of fluids retrieved using the ideal gas law (see above).

EXPERIMENTAL RESULTS

Representative mineral compositions of the solid products in selected runs are listed in Supplementary Data Table S1, and concentrations of COH molecular species in the fluid products are shown in Table 2 & Supplementary Data Table S2. Experiments employing calcite and water as starting materials, with or without the addition of quartz, synthetic chrysotile, or natural antigorite, are always characterized by significant production of CH₄-bearing aqueous fluids, showing molar ratios between CH₄ and starting calcite (CH₄/Cal_{molar}) representing the completeness of reactions ranging from ~0.13 to ~1.00 (Fig. 2; Table 2). Conversely, C-bearing species are nearly absent in comparative experiments starting with dry calcite, quartz \pm water, dry synthetic chrysotile, and dry natural antigorite separately (Supplementary Data Table S2). At run conditions, residual Ca-carbonates occur in the form of calcite (1) GPa) and aragonite (2 GPa) as identified by Raman Spectroscopy (Supplementary Data Fig. S2; see Tumiati *et al.*, 2020 for detailed methods). Graphite is never observed in the run products.

System CaO + COH

Experiments starting with calcite + water both at 1 and 2 GPa at 550 °C (24–240 h) are characterized by the growth of portlandite crystals at the expense of Cacarbonate grains (Fig. 3 & Supplementary Data Fig. S3). In experiments for 72 h, the total amounts of fluids are 49.25 μ mol at 1 GPa (run COH115) and 83.81 μ mol at 2 GPa (run COH116), in which H₂O and CH₄ are the major components whereas CO₂ and CO occur in minor amounts (Table 2). In run COH115, the concentrations of H₂O and CH₄ are 33.77 \pm 0.09 µmol (68.6 \pm 0.2 mol%) and 13.9 \pm 0.1 µmol (28.2 \pm 0.2 mol%), respectively, with X_{CH4} (=CH₄/(CH₄ + H₂O)_{molar}) of 0.292 \pm 0.002 (Table 2). The recovered fluids in run COH116 contain 56.2 \pm 0.2 µmol (68.1 \pm 0.2 mol%) H₂O and 23.7 \pm 0.2 µmol (28.7 \pm 0.3 mol%) CH₄, with X_{CH4} of 0.297 \pm 0.002 (Table 2). The CH₄/Cal_{molar} ratio at 2 GPa (0.624 \pm 0.005) is about twice that at 1 GPa (0.331 \pm 0.002), and the molar ratio between the generated total C-bearing species (including CH₄, CO₂, and CO) and starting calcite (C_{tot}/Cal_{molar}) at 2 GPa (0.69 \pm 0.05) is considerably higher than that at 1 GPa (0.37 \pm 0.02) (Fig. 2; Table 2).

To evaluate the effects of run durations, replicated experiments were performed for 24 h (run COH193) and 240 h (run COH194) at 1 GPa and 550 °C. The portlandite selvage width in run COH194 (Fig. 3d–f) is larger than that in run COH193 (Fig. 3a–c). The total amounts of fluids are 11.62 µmol in run COH193 and 27.29 µmol in run COH194, in which H₂O and CH₄ are generally dominant (Table 2). In run COH193, the concentrations of H₂O and CH₄ are 4.3 ± 0.2 µmol (39 ± 2 mol%) and 5.5 ± 0.1 µmol (51 ± 1 mol%), respectively, with X_{CH4} of 0.56 ± 0.02 (Table 2). The recovered fluids in run COH194 contain 3.4 ± 0.2 µmol (12.3 ± 0.7 mol%) H₂O and 17.4 ± 0.1 µmol (63.6 ± 0.5 mol%) CH₄, with X_{CH4} of 0.838 ± 0.009 (Table 2). Compared with the 3-day-long run COH115, the 1-day-long run COH193 has lower CH₄/Cal_{molar} and C_{tot}/Cal_{molar} ratios of 0.131 ± 0.003 and 0.16 ± 0.04, respectively, while the 10-day-long run COH194 has higher ratios of 0.413 \pm 0.003 and 0.57 \pm 0.05, respectively (Fig. 2; Table 2).

System CaO + SiO₂ + COH

Experiments starting with layered calcite + quartz + water both at 1 and 2 GPa at 550 °C (72 h) produced similar mineral assemblages mainly composed of portlandite, larnite, wollastonite, as well as residual Ca-carbonates and quartz. Larnite commonly forms a coronitic layer between portlandite and wollastonite, which in turn replace Ca-carbonates and quartz, respectively (Fig. 4). The solid products are characterized by relatively loosely packed mineral grains filled with pores, representing connected fluid pathways throughout the inner capsule (Fig. 4). The total amounts of fluids in these experiments are 44.20 µmol at 1 GPa (run COH200) and 55.60 µmol at 2 GPa (run COH125), which consist mainly of H₂O and CH₄ while CO₂ and CO occur as minor species (Table 2). In run COH200, the concentrations of H₂O and CH₄ are $23.15 \pm 0.04 \mu mol (56.0 \pm 0.1 mol\%)$ and 16.78 $\pm 0.03 \,\mu$ mol (40.60 $\pm 0.07 \,\text{mol}\%$), respectively, with X_{CH4} of 0.420 ± 0.001 (Table 2). The recovered fluids in run COH125 contain $31.79 \pm 0.06 \mu mol (60.9 \pm 0.1)$ mol%) H₂O and 17.24 \pm 0.07 µmol (33.0 \pm 0.1 mol%) CH₄, with X_{CH4} of 0.352 \pm 0.001 (Table 2). The CH₄/Cal_{molar} and C_{tot}/Cal_{molar} ratios at 2 GPa (0.663 \pm 0.003 and 0.78 \pm 0.03, respectively) are slightly higher than those at 1 GPa (0.645 \pm 0.001 and 0.70 \pm 0.02, respectively) (Fig. 2; Table 2).

System CaO + SiO₂ + MgO + COH (synthetic Cl-bearing chrysotile)

Experiments starting with layered calcite + synthetic chrysotile (containing ~1 wt% Cl) + water both at 1 and 2 GPa at 550 °C (72-264 h) generated similar solid products of mainly portlandite, larnite, and brucite (Fig. 5). At 1 GPa, portlandite and larnite grow by replacing Ca-carbonate grains, with calcite relicts and larnitehosted merwinite inclusions occasionally visible (Fig. 5a and b). At 2 GPa, by contrast, aragonite is never observed in the products (Fig. 5d-f). In these experiments, starting chrysotile has been completely consumed by newly formed phases (Fig. 5). The total amounts of fluids at 1 GPa are 58.10 µmol in run COH201 (72 h) and 39.83 µmol in run COH146 (240 h), containing mainly H₂O and CH₄ as well as minor amounts of CO₂ and CO (Table 2). In run COH201, the concentrations of H_2O and CH_4 are 33.8 \pm 0.1 μ mol (62.0 \pm 0.2 mol%) and 20.46 \pm 0.09 μ mol (37.6 \pm 0.2 mol%), respectively, with X_{CH4} of 0.377 \pm 0.002 (Table 2). In run COH146, by contrast, the concentration of H₂O decreases to $14.4 \pm 0.3 \mu$ mol $(37.4 \pm 0.7 \text{ mol}\%)$ while that of CH₄ increases to 24.0 ± 0.2 µmol (62.2 ± 0.6) mol%), with X_{CH4} of 0.625 \pm 0.007 (Table 2). The CH₄/Cal_{molar} and C_{tot}/Cal_{molar} ratios in the 3-day-long run COH201 are 0.853 ± 0.004 and 0.89 ± 0.03 , respectively, while those in the 10-day-long run COH146 are very close to 1 (Fig. 2; Table 2). Although fluid components at 2 GPa for 264 h (run COH147) show lower absolute concentrations (µmol) than those in runs COH201 and COH146, likely imputable to the partial fluid loss, their relative concentrations (mol%) are generally comparable (Table 2). In run COH147, the relative concentrations of H₂O and CH₄ are 32.9 ± 0.7 mol% and 66.4 ± 0.6 mol%, respectively, with X_{CH4} of 0.668 ± 0.007 (Table 2).

System CaO + SiO₂ + MgO + COH (natural Fe–Al-bearing antigorite)

Experiments starting with layered calcite \pm natural antigorite (containing ~4 wt% FeO and ~2 wt% Al₂O₃) + water resulted in the formation of portlandite, larnite, and brucite, together with monticellite and forsterite-rich olivine at 1 GPa and 550 °C for 72 h (Fig. 6a–c) and merwinite at 2 GPa and 550 °C for 96 h (Fig. 6d and e). Besides, Al-bearing minerals such as chlorite and vesuvianite occur in the solid products (Fig. 6c and e). In these experiments, Ca-carbonate relicts are commonly observed (Fig. 6a and d), whereas starting antigorite has been completely exhausted. The recovered fluids, with total amounts of 59.36 µmol at 1 GPa (run COH119) and 85.77 µmol at 2 GPa (run COH126), are mainly composed of H₂O and CH₄ while the concentrations of CO₂ and CO are relatively low (Table 2). In run COH119, the concentrations of H₂O and CH₄ are 38.02 ± 0.05 µmol (73.9 ± 0.1

mol%) and 11.29 \pm 0.06 µmol (21.9 \pm 0.1 mol%), respectively, with X_{CH4} of 0.229 \pm 0.001 (Table 2). In run COH126, by contrast, the concentrations of H₂O and CH₄ increase to 57.92 \pm 0.06 µmol (73.36 \pm 0.08 mol%) and 17.45 \pm 0.07 µmol (22.11 \pm 0.09 mol%), respectively, with X_{CH4} of 0.232 \pm 0.001 (Table 2). The CH₄/Cal_{molar} and C_{tot}/Cal_{molar} ratios at 2 GPa (0.759 \pm 0.003 and 0.91 \pm 0.03, respectively) are considerably higher than those at 1 GPa (0.491 \pm 0.003 and 0.58 \pm 0.02, respectively) (Fig. 2; Table 2).

Other systems

Experiments starting with calcite without added water in the inner capsule were performed to investigate whether CH₄ can be produced by dry reduction of Cacarbonates buffered by IW in the outer capsule. The solid products and starting materials in runs COH133 and COH134 show no significant difference, other than the phase transformation of calcite into aragonite at 2 GPa and 550 °C (Supplementary Data Fig. S2). Portlandite is not observed in these experiments. Run COH134 is devoid of fluids, whereas run COH133 contains very low amounts of fluid species (with a total amount of ~3 μ mol; Supplementary Data Table S2) close to the detection limit of the employed technique, likely due to the insufficient removal of adsorbed water in the inner capsule before welding.

Several CH₄-generating experiments have indicated the presence of unidentified C sources that likely result from contamination (Barbier et al., 2020 and references therein). To evaluate whether the silicate reactants were hosts for Cbearing materials representing the potential contaminants, we have conducted experiments starting with quartz \pm water, dry synthetic chrysotile, and dry natural antigorite separately. At the studied conditions, nearly no fluids were detected in experiments starting with dry quartz (runs COH135 and COH136), whereas abundant aqueous fluids (27.96 µmol) containing negligible amounts of C-bearing species were retrieved in run COH142 starting with quartz and water (Supplementary Data Table S2). At 1 GPa and 550 °C, dehydration occurred in dry experiments starting with synthetic chrysotile (run COH195) and natural antigorite (run COH137) separately (e.g. Padrón-Navarta et al., 2013; Shen et al., 2015), resulting in the production of olivine (Supplementary Data Fig. S4) and abundant aqueous fluids (15.03 µmol and 68.35 µmol, respectively; Supplementary Data Table S2). In run COH195 starting with 3.60 mg of synthetic chrysotile, the fluid products contain small amounts of C-bearing species (with a total amount of ~3 umol; Supplementary Data Table S2), probably indicative of minor C contents in the reactants. In this scenario, the lower amounts of starting chrysotile employed in runs COH201 and COH146 (0.80 mg and 0.90 mg, respectively) may have contributed at most only ~0.7 µmol of C-bearing species to the fluid products. In

run COH137, by contrast, C-bearing species are almost absent in the fluid products (Supplementary Data Table S2), reflecting nearly no C-bearing materials hosted in natural antigorite. Thus, we can conclude that C contents in the silicate reactants are insignificant and they have negligible effects on the obtained fluid compositions.

THERMODYNAMIC MODELLING

Assuming equilibrium conditions, the conventional Perple_X modelling was conducted to predict mainly solid phases, while the Deep Earth Water (DEW) model was used to calculate primarily aqueous fluids. Although both of them rely on thermodynamics, the DEW model in particular the EQ6 reaction path code can deal with the evolution of a water/rock system as the reaction progress, which is useful to investigate the kinetics of Ca-carbonate aqueous reduction into CH₄.

Conventional model

To compare phases generated in the experiments with those predicted under equilibrium conditions, as well as to investigate equilibrated phases under a wide range of fO_2 and fH_2 conditions, we calculated $\log fO_2$ -log fH_2 diagrams in the CaO + COH, CaO + SiO₂ + COH, and CaO + SiO₂ + MgO + COH systems both at 1 and 2 GPa at 550 °C, employing the Perple_X software package (version 6.8.7; Connolly, 2005) and the internally consistent thermodynamic database of Holland

& Powell (1998) revised in 2004 (hp04ver.dat). As thermodynamic parameters of wüstite and portlandite are currently not available in this database, we added them mostly from Robie & Hemingway (1995). Solid phases were taken to be pure in the calculations while COH molecular species were described by a generic hybrid fluid EoS with non-linear subdivision (COH-Fluid+; Connolly & Galvez, 2018). The hematite-magnetite (HM), FMQ, IW, and quartz-iron-fayalite (QIF) buffers are shown for reference, corresponding to log fO_2 values of -16.9, -20.5, -26.0, and -27.8 at 1 GPa and 550 °C, and -16.7, -19.4, -25.3, and -27.2 at 2 GPa and 550 ^oC, respectively. The "fluids" routine (H–O MRK hybrid–EoS) of the Perple_X software was used to calculate fH_2 conditions in the outer capsule containing IW + H₂O, showing log *f*H₂ values of 4.2 (1 GPa and 550 °C) and 4.9 (2 GPa and 550 °C) identical to those in the inner capsule due to H_2 permeability of the Au₆₀Pd₄₀ alloy (see Section *Experimental Methods*). Compared with the well-constrained fO_2 and fH_2 conditions in the outer capsule (red cross in Fig. 7), fO_2 values in the inner capsule are slightly lower than fO_2^{IW} where fluids mainly consist of CH₄ and H₂O rather than pure water (see Section Experimental Methods).

System CaO + COH

The CH₄-bearing fluids remain stable at log $fO_2 < -24.0$ and log $fH_2 > 2.7$ at 1 GPa and 550 °C, and log $fO_2 < -23.2$ and log $fH_2 > 3.6$ at 2 GPa and 550 °C (Fig. 7a and

b). In contrast, CH_4 -bearing fluids would be replaced by H_2O -rich fluids containing minor amounts of CO_2 with increasing fO_2 conditions, whereas Ca-carbonates and/or graphite would become the dominant C-bearing species with decreasing fH_2 conditions (Fig. 7a and b). At run conditions, the equilibrated phase assemblages are portlandite and CH_4 -bearing fluids, indicating the fH_2 -dependent Ca-carbonate reduction reaction:

$$CaCO_3 + 4H_2 = Ca(OH)_2 + CH_4 + H_2O.$$
 (2)

Overall, these calculations are in agreement with the experimental results, as portlandite and CH₄-bearing fluids are the major products in runs COH193, COH115, COH194, and COH116 (Fig. 3 & Supplementary Data Fig. S3; Table 2). However, relicts of Ca-carbonate reactants are commonly observed in these experiments (Fig. 3; Supplementary Data Fig. S3), suggesting the incomplete reduction processes (see Section *Discussion*).

System $CaO + SiO_2 + COE$

At run conditions for these layered experiments, chemical gradients have been preserved in the inner capsule, which are favorable for investigating the kinetics of Ca-carbonate aqueous reduction into CH_4 (see Section *Experimental Methods*). To compare experimental run products with phases predicted under equilibrium conditions in a sliding compositional space, we calculated log fO_2 – X_{CaCO3} (=CaCO₃/(CaCO₃ + SiO₂)_{molar}) diagrams at constant log *f*H₂ values of 4.2 at 1 GPa and 550 °C (Supplementary Data Fig. S5a) and 4.9 at 2 GPa and 550 °C (Supplementary Data Fig. S5b), corresponding to the IW buffer. These diagrams suggest that the equilibrated phase assemblages vary with X_{CaCO3} values under the studied *P*-*T*-*f*O₂ conditions, ranging from portlandite + larnite + CH₄-bearing fluids (1 > X_{CaCO3} > ~0.67), to larnite + wollastonite + CH₄-bearing fluids (~0.67 > X_{CaCO3} > ~0.50), and to wollastonite + quartz + CH₄-bearing fluids (~0.50 > X_{CaCO3} > 0; Supplementary Data Fig. S5). Further, we calculated representative log *f*O₂-log *f*H₂ diagrams at the fixed CaCO₃ and SiO₂ molar ratio of 3:2 both at 1 and 2 GPa at 550 °C (Fig. 7c and d).

The CH₄-bearing fluids remain stable at log $fO_2 < -22.7$ and log $fH_2 > 2.7$ at 1 GPa and 550 °C, and log $fO_2 < -22.4$ and log $fH_2 > 3.6$ at 2 GPa and 550 °C (Fig. 7c and d). In contrast, CH₄-bearing fluids would be replaced by H₂O-rich fluids containing minor amounts of CO₂ with increasing fO_2 conditions, whereas Cacarbonates and/or graphite would become the dominant C-bearing species with decreasing fH_2 conditions (Fig. 7c and d). At run conditions, the equilibrated phase assemblages are larnite, wollastonite, and CH₄-bearing fluids, indicating the fH_2 -dependent Ca-carbonate reduction reaction:

$$3CaCO_3 + 2SiO_2 + 12H_2 = Ca_2SiO_4 + CaSiO_3 + 3CH_4 + 6H_2O.$$
 (3)

At the studied conditions, phases predicted by thermodynamic modelling (Fig. 7c and d; Supplementary Data Fig. S5) are not in accord with experimental products generated in runs COH200 and COH125 (Fig. 4; Table 2). Moreover, starting Ca-carbonates and quartz commonly appear as relicts in these experiments (Fig. 4), suggesting the incomplete reduction processes (see Section *Discussion*).

$System CaO + SiO_2 + MgO + COH$

Similar to calculations performed in the CaO + SiO₂ + COH system, log fO_2 - X'_{CaCO3} (=CaCO₃/(CaCO₃ + Mg₃Si₂O₅(OH)₄)_{molar}) diagrams were calculated at constant log *f*H₂ values of 4.2 at 1 GPa and 550 °C (Supplementary Data Fig. S6a) and 4.9 at 2 GPa and 550 °C (Supplementary Data Fig. S6b), corresponding to the IW buffer. These diagrams suggest that X'_{CaCO3} values play an important role in regulating the equilibrated phase assemblages under the studied $P-T-fO_2$ conditions. At 1 GPa for $X'_{CaCO3} > \sim 0.67$, the equilibrated phase assemblages are portlandite + merwinite + brucite + CH₄-bearing fluids ($1 > X'_{CaCO3} > \sim 0.75$) and monticellite + merwinite + brucite + CH₄-bearing fluids ($\sim 0.75 > X'_{CaCO3} > \sim 0.67$; Supplementary Data Fig. S6a). At 2 GPa for $X'_{CaCO3} > \sim 0.75$, the equilibrated phase assemblages are portlandite + larnite + brucite + CH_4 -bearing fluids (1 > X'_{CaCO3} > ~0.80) and larnite + merwinite + brucite + CH₄-bearing fluids (~ $0.80 > X'_{CaCO3} >$ ~0.75; Supplementary Data Fig. S6b). Further, we calculated representative log

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 fO_2 -log fH_2 diagrams at the fixed CaCO₃ and Mg₃Si₂O₅(OH)₄ molar ratio of 9:1 both at 1 and 2 GPa at 550 °C (Fig. 7e and f).

The CH₄-bearing fluids remain stable at log $fO_2 < -22.8$ and log $fH_2 > 2.7$ at 1 GPa and 550 °C, and log $fO_2 < -22.6$ and log $fH_2 > 3.6$ at 2 GPa and 550 °C (Fig. 7e and f). In contrast, CH₄-bearing fluids would be replaced by H₂O-rich fluids containing minor amounts of CO₂ with increasing fO_2 conditions, whereas Cacarbonates and/or graphite would become the dominant C-bearing species with decreasing fH_2 conditions (Fig. 7e and f). At run conditions, the equilibrated phase assemblages are portlandite + merwinite + brucite + CH₄-bearing fluids (1 GPa) and portlandite + larnite + brucite + CH₄-bearing fluids (2 GPa), indicating the fH_2 -dependent Ca-carbonate reduction reactions:

$$9CaCO_{3} + Mg_{3}Si_{2}O_{5}(OH)_{4} + 36H_{2} =$$

$$6Ca(OH)_{2} + Ca_{3}Mg(SiO_{4})_{2} + 2Mg(OH)_{2} + 9CH_{4} + 12H_{2}O,$$
(4)

and

$$9CaCO_{3} + Mg_{3}Si_{2}O_{5}(OH)_{4} + 36H_{2} =$$

$$5Ca(OH)_{2} + 2Ca_{2}SiO_{4} + 3Mg(OH)_{2} + 9CH_{4} + 12H_{2}O.$$
(5)

At the studied conditions of 1 GPa, thermodynamically predicted phases (Fig. 7e; Supplementary Data Fig. S6a) are not in agreement with experimentally generated products in runs COH201 and COH146 (Fig. 5a–c; Table 2). By contrast, the assemblage of portlandite + larnite + brucite + CH_4 -bearing fluids produced in

run COH147 (Fig. 5d–f; Table 2) has been predicted by thermodynamic modelling at 2 GPa (Fig. 7f; Supplementary Data Fig. S6b). In particular, relicts of Cacarbonate reactants have been rarely or never observed in runs COH146 and COH147 characterized by long run durations (Fig. 5), suggesting that the reduction processes are almost complete (see Section *Discussion*).

DEW model in the CaO + COH system

To investigate the reaction progress of Ca-carbonate aqueous reduction under the studied conditions, we performed thermodynamic calculations in the representative CaO + COH system using the DEW model (Sverjensky *et al.*, 2014; Huang & Sverjensky, 2019) and the EQ3/EQ6 software (Wolery, 1992; Wolery & Daveler, 1992) with a modified Berman database (Berman, 1988). The speciation–solubility code EQ3 was used to calculate reduced fluid compositions at P = 1 GPa, T = 550 °C, and log $fO_2 = -26.0$ corresponding to the IW buffer, where C molalities were set to make the fluids saturated with portlandite. At the same P-T conditions, the reaction path modelling code EQ6 was further used to model the interactions between the EQ3 fluids containing 1.0 kg of H₂O and a given number of calculate at different F/R ratios of 0.5 and 2, while their results are nearly identical.

The evolution of minerals, dissolved elements and species in the fluids, and fO_2 and fH_2 conditions as a function of the reaction progress (in logarithm) at 1 GPa and 550 °C for the F/R ratio of 2 is shown in Fig. 8. The reaction proceeds with the progressive growth of portlandite by replacing calcite, where calcite reactant is completely consumed as the reaction nears completion (Fig. 8a). The dissolved C and Ca contents in the fluids remain almost unchanged at the onset of the reaction, while they start to increase at log reaction progress of about -2.5 and 0, respectively (Fig. 8b). The model predicts high relative concentrations of CH₄ in the fluids, and its evolution during the reaction is similar to that of the dissolved C (Fig. 8b and c). When the reaction is close to completion, concentrations of aqueous C-bearing species significantly increase in the fluids, including CH₄, HCOO⁻, CH₃COO⁻, CO, CO₂, H₂CO₃, HCO₃⁻, and CO₃²⁻ (Fig. 8c). The initial fO₂ of the IW buffer, as well as H_2 , remains nearly unchanged until at reaction completion when the former increases to log $fO_2 \approx -23.0$ ($\Delta FMQ \approx -3$) while the latter decreases to log $fH_2 \approx 2.7$ (Fig. 8d). As a result, the evolution at log reaction progress higher than ~0 is characterized by an increase in fO_2 but a decrease in fH_2 , contributing to portlandite growth at the expense of calcite, and the elevated molalities of dissolved C and Ca elements as well as aqueous C-bearing species in the fluids (Fig. 8). In this study, however, the double capsule technique has fixed fH_2 (and thus fO_2) conditions throughout the experiments (see Section *Experimental* *Methods*), indicating that the reduction processes proceed at log reaction progress lower than ~0 (Fig. 8).

DISCUSSION

Comparison between experimental and thermodynamic modelling results

In this study, Ca-carbonate reactants commonly occur as relicts in the run products, particularly in experiments starting with calcite + water, calcite + quartz + water, and calcite + natural antigorite + water (Figs. 3, 4 and 6). However, phase assemblages predicted by thermodynamic modelling at run conditions indicate that Ca-carbonates would be metastable if equilibrium were reached in these experiments (Fig. 7 and 8a). Since the IW buffer constrained fH_2 values in both inner and outer capsules throughout the runs (see Section Experimental Methods), the incomplete consumption of Ca-carbonates in the presence of reduced fluids (Table 2) is likely attributed to short run durations. Although the intermediate products in the layered experiments have potentially hindered further reactions between Ca-carbonates and silicates especially in the CaO + SiO_2 + COH system, the fluids can flow throughout the inner capsule as reflected by the relatively loosely packed mineral grains filled with pores (Fig. 4). In this scenario, CH₄ production may proceed firstly in the $CaO + SiO_2 + COH$ system and subsequently in the CaO + COH system, which does not considerably affect our discussion below with respect to the kinetics-controlled Ca-carbonate aqueous reduction into CH_4 . At 1 GPa and 550 °C, thermodynamic calculations in the CaO + SiO₂ + MgO + COH system demonstrate that the equilibrated phase assemblage is comprised of portlandite, merwinite, brucite, and CH₄-bearing fluids (Fig. 7e). In contrast, products in runs COH201 and COH146 are mainly composed of portlandite, larnite, brucite, and CH₄-bearing fluids, as well as calcite relicts, whereas merwinite appears as inclusions in larnite commonly intergrown with brucite (Fig. 5a–c). These thermodynamic constraints and microstructures suggest that merwinite in these experiments may have been largely consumed by calcite to form larnite and brucite:

$$Ca_{3}Mg(SiO_{4})_{2} + CaCO_{3} + 4H_{2} =$$

$$2Ca_{2}SiO_{4} + Mg(OH)_{2} + CH_{4} + H_{2}O.$$
(6)

Based on the negligible calcite relicts in run COH146, as well as its CH_4/Cal_{molar} ratio of ~1, the newly formed phase assemblage of portlandite + larnite + brucite + CH_4 -bearing fluids may have been close to re-equilibrium, as reflected by the long run duration of 240 h for the experiment. At 2 GPa and 550 °C, the phase assemblage of portlandite + larnite + brucite + CH_4 -bearing fluids generated in run COH147 is consistent with that predicted by thermodynamic modelling in the CaO + SiO_2 + MgO + COH system (Fig. 7f), suggesting that equilibrium was almost attained in the experiment. This is in agreement with the long run duration of 264 h

for run COH147 causing the complete consumption of Ca-carbonate reactant (Fig. 5d–f).

Kinetics-controlled Ca-carbonate aqueous reduction into CH₄

Overall, comparisons of experimental run products with thermodynamically predicted phase assemblages indicate that equilibrium has not yet been attained in most of the studied runs (see above). Time-series experiments conducted in representative systems at 1 GPa and 550 °C provide evidence for the durationcontrolled Ca-carbonate aqueous reduction into CH₄, with the CH₄/Cal_{molar} ratios ranging from ~0.13 at 24 h (run COH193), to ~0.33 at 72 h (run COH115), and to ~0.41 at 240 h (run COH194) in the CaO + COH system, and from ~0.85 at 72 h (run COH201) to ~1.00 at 240 h (run COH146) in the CaO + SiO_2 + MgO + COH (synthetic Cl-bearing chrysotile) system (Fig. 2; Table 2). Based on these ratios, we have retrieved rate constants of 0.8×10^{-6} s⁻¹ and 7.4×10^{-6} s⁻¹ for such kineticscontrolled reactions in the CaO + COH and CaO + SiO_2 + MgO + COH (synthetic Cl-bearing chrysotile) systems, respectively (Fig. 9). For comparison, the rate constants of 4.0×10^{-6} s⁻¹ and 2.6×10^{-6} s⁻¹ were also calculated for reactions in the $CaO + SiO_2 + COH$ and $CaO + SiO_2 + MgO + COH$ (natural Fe–Al-bearing) antigorite) systems, respectively, despite their limited experimental data (Fig. 9). These constraints demonstrate that equilibrium can be nearly attained at run durations of ~2400 h, ~500 h, ~250 h, and ~750 h in experiments starting with calcite + water, calcite + quartz + water, calcite + synthetic chrysotile + water, and calcite + natural antigorite + water, respectively (Fig. 9).

At 1 GPa and 550 °C, the CH₄/Cal_{molar} ratios in experiments starting with calcite + quartz + water (run COH200), calcite + synthetic chrysotile + water (run COH201), and calcite + natural antigorite + water (run COH119) are higher than the ratio in run COH115 starting with calcite + water at the same run duration of 72 h (Fig. 2), indicating that addition of silicates can potentially enhance the efficiency of calcite reduction into CH₄. At these conditions, the calculated rate constants for the silicate-involving reactions are about 3-9 times higher than the constant for the silicate-absent reaction (Fig. 9). In contrast to run COH200, the relatively lower CH₄/Cal_{molar} ratio in run COH119 is probably because starting antigorite contains small amounts of Fe^{3+} (Vitale Brovarone *et al.*, 2017), thereby leading to fO_2 slightly higher than the IW buffer responsible for the reduction processes. Conversely, the relatively higher CH₄/Cal_{molar} ratio in run COH201 is probably attributed to the incorporation of ~1 wt% Cl in starting chrysotile during its synthesis (Villa et al., 2018), which may increase the aqueous solubility of calcite (Newton & Manning, 2002) and thus promote CH_4 generation through Reaction (7): $CaCO_3 + 2Cl^2 + 4H_2 = CaCl_2 + 2OH^2 + CH_4 + H_2O_1$ (7)

and/or Reaction (8):

$$CaCO_3 + Cl^- + 4H_2 = CaCl^+ + 2OH^- + CH_4 + H_2O.$$
 (8)

The acceleration of Ca-carbonate aqueous reduction in the presence of silicates has also been recorded at 2 GPa and 550 °C by comparing the CH₄/Cal_{molar} ratios in runs COH116 and COH125 with the same run duration of 72 h, whereas the longer duration of 96 h for run COH126 may compensate for the negative effects of Fe³⁺ in starting antigorite (Vitale Brovarone et al., 2017) and thus contribute to its higher CH₄/Cal_{molar} ratio (Fig. 2). The positive role of silicates in these reduction processes is inferred to be mainly associated with the dissolved SiO₂ in aqueous fluids (Tumiati et al., 2017, 2020), which has promoted Ca-carbonate dissolution through synthesizing Ca–Si-bearing complexes (e.g. $Ca(HSiO_3)^+$; Huang & Sverjensky, 2019) and thus accelerated CH₄ production. In contrast, Ca–Mgbearing complexes are relatively hard to be synthesized in the fluids, indicating that the MgO component in serpentines may have not significantly affected the reduction efficiency of Ca-carbonates. Besides the addition of silicates, an increase in pressures is also favorable for Ca-carbonate reduction into CH₄ at comparable run conditions (cf. runs COH115 and COH116, runs COH200 and COH125, and runs COH119 and COH126), despite their variable accelerating trends (Fig. 2). This is probably related to Ca-carbonate aqueous solubility increasing with pressures under subduction zone conditions (e.g. Newton & Manning, 2002; Caciagli & Manning, 2003). However, since experiments in this study were only performed at a fixed temperature of 550 $^{\circ}$ C, the potential effects of variable temperatures on HP aqueous reduction of Ca-carbonates would be beyond the scope of discussion.

Stability of CH₄ and/or graphite through HP aqueous reduction of C-bearing materials

The experimental and thermodynamic modelling results suggest that products contain copious amounts of CH₄-bearing fluids while graphite is never observed at run conditions (see above). The current study, together with other reduction experiments starting with carbonate minerals or organic matter (e.g. carboxylic acids and carboxylates) and water at variable oxygen buffers (Sharma et al., 2009; Lazar et al., 2014; Li, 2017; Mukhina et al., 2017), demonstrates the strong dependence of CH_4 and graphite stabilities on fO_2 under subduction zone conditions (Fig. 10). It is apparent that CH_4 (with or without other short-chain hydrocarbons), relative to graphite, is the dominant C-bearing species at low fO_2 buffered by Fe, IW/IM, or WM under a wide range of P-T conditions (Fig. 10). At increasing fO₂ buffered by Co–CoO or Ni–NiO, by contrast, decomposition of carbonate minerals or organic matter would result in the concomitant formation of CH₄ and graphite (Fig. 10). This is in agreement with field-based studies showing the coexistence of CH₄ and graphite through Fe-bearing dolomite aqueous reduction at Δ FMQ -2.5 to -1.5 at 2.5-3.0 GPa and 500-575 °C (between the WM and Co-CoO buffers) in carbonated eclogites from the Chinese southwestern Tianshan (Tao et al., 2018) and calcite methanation induced by H₂-riched fluids at Δ FMQ -6.0 to -3.0 at 1.0-2.0 GPa and 400-500 °C (between the WM and Co-CoO buffers) in ophicalcites from the Italian Western Alps (Vitale Brovarone et al., 2017; Giuntoli et al., 2020). At more oxidized conditions buffered by Re-ReO₂, decomposition of carbonate minerals or organic matter would be characterized by the precipitation of graphite but the absence of CH₄ (Fig. 10). Thus, these experiments suggest that HP aqueous reduction of carbonate minerals or organic matter buffered by WM or below may generate CH₄ (possibly with other shortchain hydrocarbons) as the dominant C-bearing species, which would be gradually replaced by graphite with the increasing fO_2 . Nevertheless, due to the lack of experiments on HP aqueous reduction of C-bearing materials at fO_2 above the WM buffer at relatively lower temperatures (e.g. < 600 °C), it is undetermined whether CH₄ and/or graphite can remain stable under these conditions.

The absence of graphite through HP aqueous reduction of carbonate minerals or organic matter at low fO_2 (Fig. 10) is probably due to the coupled fO_2 and fH_2 in a closed hydrous system, in which low fO_2 represents high fH_2 that may promote the hydrogenation of graphite forming CH₄ (e.g. Sharma *et al.*, 2009; Vitale Brovarone *et al.*, 2017; Peña-Alvarez *et al.*, 2021). To further investigate the dependence of graphite stability on fO_2 in a nearly anhydrous system, we calculated log fO_2 –*P* diagrams at very low fH_2 (e.g. log $fH_2 = -2.0$) and a fixed temperature of 550 °C in the CaO + C, CaO + SiO₂ + C, and CaO + SiO₂ + MgO + C systems. In the CaO + C system, the onset of graphite precipitation through Ca-carbonate anhydrous reduction happens at fO_2 below the IW buffer but close to the QIF buffer under the studied *P*–*T* conditions (Supplementary Data Fig. S7a). In contrast, calculations in the CaO + SiO₂ + C and CaO + SiO₂ + MgO + C systems at representative starting compositions suggest that anhydrous graphitization of Cacarbonates starts at Δ FMQ –2 to –1 under the studied *P*–*T* conditions (Supplementary Data Fig. S7b and c). However, these calculations are relatively hard to be confirmed experimentally, where extremely long run durations would be required due to the lack of fluid medium (e.g. Holloway & Wood, 1988).

Geological implications

Our data provide experimental evidence for kinetics-controlled abiotic CH_4 production through Ca-carbonate reduction in the CaO + COH, CaO + SiO₂ + COH, and CaO + SiO₂ + MgO + COH systems under subduction zone *P*–*T* conditions, induced by aqueous fluids at low fO_2 close to the IW buffer. In natural subduction zone settings, however, the redox nature of slab-derived fluids remains largely controversial. Taking subducted serpentinites as an example, rock-based studies, theoretical calculations, and experimental simulations suggest that dehydration of these rocks at eclogite facies may generate highly oxidized fluids (Debret et al., 2014, 2015; Debret & Sverjensky, 2017; Maurice et al., 2020). In contrast, petrological investigation and thermodynamic modelling demonstrate that reduced fluids containing H₂ or H₂S can be released during prograde deserpentinization (Peretti et al., 1992; Piccoli et al., 2019). Redox states of the fluids liberated from subducted serpentinites are inferred to depend on a combination of factors, including the hydration extent of their protoliths before entering subduction zones (Evans et al., 2017; Evans & Frost, 2021). Subducted serpentinites experiencing intense pre-subduction seawater alteration discharge oxidized fluids in equilibrium with mainly magnetite, whereas those recording less pervasive seawater-rock interactions release reduced fluids that are equilibrated with both awaruite (FeNi₃) and magnetite corresponding to the IM buffer (Carbonin et al., 2015). Therefore, dehydration of subducted serpentinites can potentially liberate highly reduced fluids. Other than deserpentinization, HP serpentinization of ultramafic rocks at depths of or greater than 20-30 km in subduction zones, as suggested by natural observations and thermodynamic calculations, may also represent a possible source of reduced fluids that commonly contain some amounts of H₂ (Li et al., 2007, 2010; Vitale Brovarone et al., 2017, 2020; Lazar, 2020). An infiltration of such reduced fluids derived from deserpentinization or serpentinization at forearc depths would

be conducive to aqueous reduction of subducted Ca-carbonates into CH₄, thereby providing potential insights into C mobility in subduction zones.

At 1 GPa and 550 °C, the reaction rate constant retrieved in the CaO + COH system indicates that equilibrium can be nearly attained at the run duration of \sim 2400 h, while the addition of silicates would reduce the durations required for equilibrium to less than ~750 h (Fig. 9). Thus, silicate involvement can enhance the reduction efficiency at relatively short durations of several months before the complete consumption of Ca-carbonate reactants. At longer durations, the kineticscontrolled reduction processes of Ca-carbonates would reach equilibrium, leading to their molar ratios between CH₄ and starting calcite representing the reaction progress consistent with those containing silicate reactants (Fig. 9). Nevertheless, Ca-carbonate reactants are commonly preserved in natural HP reduced rocks (e.g. CH₄-bearing ophicalcites from the Italian Western Alps; Vitale Brovarone et al., 2017; Giuntoli et al., 2020), indicative of the incomplete Ca-carbonate reduction into CH₄ at convergent margins. The overall slab dehydration processes are considered to be continuous over millions of years under a wide range of P-Tconditions, whereas the individual fluid flow events in subduction zones may be much faster and highly channelized (John et al., 2012). These slab-derived fluids are mobilized in a short-lived and pulse-like character, as indicated by lithium chronometry, corresponding to timescales of the fluid-rock interactions as short as

hundreds of years to several months (Penniston-Dorland et al., 2010; John et al., 2012; Taetz et al., 2018). Furthermore, natural reaction rates, especially in regional metamorphic environments, are regarded as slower than those predicted by laboratory experiments (Baxter, 2003; Baxter & Depaolo, 2004). In this scenario, the experimentally constrained durations required for equilibrium (Fig. 9) may underestimate the amounts of time for the completion of fluid-rock interactions in natural subduction zone settings (e.g. Penniston-Dorland et al., 2010). Besides the addition of silicates, an increase in pressures can also enhance the reduction efficiency of Ca-carbonates as reactions proceed (Fig. 2). As a result, our experimental data provide potential implications for short-lived fluid-rock interactions in subduction zones, where the production of CH4 through kineticscontrolled Ca-carbonate aqueous reduction may be accelerated by involving silicates and/or increasing pressures. However, uncertainties remain regarding the widespread application of the experimentally constrained kinetic models to natural settings, considering the variability in fluid compositions and fluid to rock ratios at convergent margins (e.g. Sieber et al., 2020).

CONCLUSIONS

By using calcite + water \pm quartz \pm serpentine (synthetic Cl-bearing chrysotile and natural Fe–Al-bearing antigorite) as starting materials, we have performed

experiments on kinetics-controlled Ca-carbonate aqueous reduction into CH₄ in the CaO + COH, $CaO + SiO_2 + COH$, and $CaO + SiO_2 + MgO + COH$ systems buffered by IW both at 1 and 2 GPa at 550 °C. Experimental run products contain portlandite ± larnite ± wollastonite ± brucite as well as Ca-carbonate and/or silicate reactants, and copious amounts of CH₄-bearing aqueous fluids characterized by variable molar ratios between CH₄ and starting calcite (CH₄/Cal_{mol} = -0.13 to -1.00) reflecting different degrees of reaction completion. Thermodynamic calculations demonstrate that equilibrium has not yet been attained in most of the studied runs, while reaction kinetics play an important role in controlling these reduction processes as evidenced by time-series experiments. The retrieved rate constants for reactions in the SiO₂-bearing systems are about 3–9 times higher than the constant in the CaO + COH system ($0.8 \times 10^{-6} \text{ s}^{-1}$), suggesting that the addition of silicates can considerably shorten the durations required for equilibrium of Ca-carbonate aqueous reduction. As reactions proceed, an increase in pressures is also favorable for the production of CH₄. Our work indicates that Ca-carbonate reduction at forearc depths, triggered by aqueous fluids at fO_2 of IW, represents a possible source of abiotic CH₄ in subduction zones and thus provides potential insights into the mobility of subducted C. The reduction efficiency can be enhanced by involving silicates and/or increasing pressures in particular through the short-lived fluid-rock interactions.

DATA AVAILABILITY

The data underlying this article are available in the article and in its online supplementary material.

SUPPLEMENTARY DATA

Supplementary data are available at Journal of Petrology online.

FUNDING

This work was supported by the National Key Research and Development Program of China (No. 2019YFA0708501), by an Italian program MIUR PRIN (No. 2017ZE49E7_002) and MIUR Levi Montalcini, and by a Richard Lounsbery Foundation grant. This work is part of a project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 864045). Carla Tiraboschi acknowledges support from the German Research Foundation (DFG Grant TI 1078/2-1).

ACKNOWLEDGEMENTS

We thank Marcello Campione and Chiara Groppo for providing synthetic chrysotile and natural antigorite, respectively. We are grateful to Andrea Risplendente for his assistance during microprobe analysis and to Andrea Amalfa for preparing some of the experiments. The authors wish to acknowledge Matthieu Galvez, Melanie Sieber, and Codi Lazar for their detailed and constructive comments that have substantially improved the manuscript. Jörg Hermann is greatly appreciated for his editorial handling and helpful suggestions.

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Phase	Formula ¹	Abbreviation ^{II}
Antigorite	$Mg_{x(48-4y)}Fe_{(1-x)(48-4y)}Al_{8y}Si_{34-4y}O_{85}(OH)_{62}$	Atg
Aragonite	CaCO ₃	Arg
Brucite	Mg(OH) ₂	Brc
Calcite	CaCO ₃	Cal
Carbon dioxide	CO ₂	-
Carbon monoxide	СО	
Chlorite	$Mg_{x(6-y)}Fe_{(1-x)(6-y)}Al_{2y}Si_{4-y}O_{10}(OH)_{8}$	Chl
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	Ctl
Diopside	CaMgSi ₂ O ₆	Di
Dolomite	CaMg(CO ₃) ₂	Dol
Fayalite	Fe ₂ SiO ₄	Fa
Forsterite	Mg ₂ SiO ₄	Fo
Graphite	С	Gr
Hematite	Fe ₂ O ₃	Hem
Hydrogen	H ₂	_
Iron	Fe	_
Larnite	Ca ₂ SiO ₄	Lrn
Lime	CaO	_
Magnetite	Fe ₃ O ₄	Mag
Methane	CH4	_
Merwinite	Ca ₃ Mg(SiO ₄) ₂	Mw
Monticellite	CaMgSiO ₄	Mtc
Olivine	(Mg,Fe) ₂ SiO ₄	Ol
Oxygen	O ₂	_
Periclase	MgO	Per
Portlandite	Ca(OH) ₂	Port
Quartz	SiO ₂	Q
Spurrite	Ca ₅ (SiO ₄) ₂ CO ₃	Spu
Vesuvianite	Ca ₁₉ (Mg,Fe,Al) ₁₃ Si ₁₈ O ₆₈ (OH,F,O) ₁₀	Ves
Water	H ₂ O	-
Wollastonite	CaSiO ₃	Wo
Wüstite	FeO	Wus

Table 1: Chemical formulas and abbreviations of phases in this study

¹ Formulas of antigorite and chlorite are from Padrón-Navarta *et al.* (2013) while vesuvianite from Groat *et al.*

(1992).

^{II}Abbreviations are mostly from Whitney & Evans (2010).

Run	P		Starting	Compo	sition of	starting	material	X _C	Time	Solid product	
(GP (°C a))		material	$(mg/\mu mol)$						(h)	S	
				Cui	Y	Cu	mg	1120			
System CaO + COH											
COH	1	550	Cal, H ₂ O	4.20/	_	_	-	1.20/	1.0	24	Port, Cal
193				42.0				66.6	0	Y	
COH	1	550	Cal, H ₂ O	4.20/	_	_	—	1.00/	1.0	72	Port, Cal
115				42.0				55.5	0		
COH	1	550	Cal, H ₂ O	4.20/	-	_	-	1.30/	1.0	240	Port, Cal
194				42.0				72.2	0		
COH	2	550	Cal, H_2O	3.80/	-	-	$-\lambda$	1.00/	1.0	72	Port, Arg
116				38.0			\mathbf{N}	55.5	0		
System $CaO + SiO_2 + COH$											
COH	1	550	Cal, O,	2.60/	2.60/		-	0.80/	0.3	72	Port, Lrn, Wo, Cal,
200			H ₂ O	26.0	43.3)		44.4	8		Q
COH	2	550	Cal, Q,	2.60/	2.00/	_	—	0.90/	0.4	72	Port, Lrn, Wo, Arg,
125			H ₂ O	26.0	33.3			50.0	4		Q
COH	2	550	Cal, Q,	2.10/	2.80/	_	_	0.90/	0.3	72	Port, Lrn, Wo, Arg,
121			H ₂ O	21.0	46.6			50.0	1		Q
System	CaO +	SiO ₂ -	+ MgO + CO	H (synth	netic Cl-ł	pearing o	chrysotile	e)			
COH	1	550	Cal Ctl	2.40/	_	0.80/	_	0.90/	0.8	72	Port Lrn Brc Mw
201	1	~	H_2O	24.0		2.90		50.0	9	, _	Cal
COH	1	550	Cal. Ctl.	2.40/	_	0.90/	_	1.00/	0.8	240	Port. Lrn. Brc. Mw.
146			H ₂ O	24.0		3.26		55.5	8		Cal
COH	2	550	Cal, Ctl,	2.80/	-	1.40/	—	1.10/	0.8	264	Port, Lrn, Brc
147		/	H_2O	28.0		5.07		61.1	5		
System $CaO + SiO_2 + MgO + COH$ (natural Fe–Al-bearing antigorite)											
COH	1	550	Cal. Atg.	2.30/	_	_	0.79/	1.00/	0.9	72	Port, Lrn, Brc, Mtc.
119			H_2O	23.0			0.17	55.5	9		Ol, Chl, Cal
СОН	2	550	Cal, Atg.	2.30/	_	_	1.30/	0.90/	0.9	96	Port, Lrn, Brc, Mw.
			,							-	, , , , , , , , , , , , , , , , , , , ,

Run	Tot	Conce	ntration	of flui	d	Concentration of fluid				<i>Х</i> _{СН4} п	CH ₄ /Cal	C _{tot} /Cal
	al	species (µmol)				specie	s (mol%	5)			Ⅲ molar	IV molar
	flui	H_2O	CH_4	CO_2	CO	H_2O	CH_4	CO_2	CO			
	d											
System CaO + COH												
COH	11.6	4.3(2	5.5(1	0.00	1(2	39(2	51(1	0.0(10(0.56(0.131(3)	0.16(4)
193	2))	(9))))	8)	15)	2)	Ć	
COH	49.2	33.7	13.9(0.31	1.3	68.6(28.2(0.6(3(1)	0.29	0.331(2)	0.37(2)
115	5	7(9)	1)	(8)	(7)	2)	2)	2)		2(2)		
COH	27.2	3.4(2	17.4(0.0(7(2	12.3(63.6(0.0(24(0.83	0.413(3)	0.57(5)
194	9)	1)	1))	7)	5)	4)	7)	8(9)		
COH	83.8	56.2(23.7(0.5(2(2	68.1(28.7(0.7(3(2)	0.29	0.624(5)	0.69(5)
116	1	2)	2)	2))	2)	3)	2)		7(2)		
System $CaO + SiO_2 + COH$											1	
COH	44.2	23.1	16.7	0.09	1.3	56.0(40.6	0.22	3.1(0.42	0.645(1)	0.70(2)
200	0	5(4)	8(3)	(2)	(4)	1)	0(7)	(5)	9)	0(1)	01010(1)	0.10(2)
COH	55.6	31.7	17.2	0.14	3.0	60.9(33.0(0.3(6(1)	0.35	0.663(3)	0.78(3)
125	0	9(6)	4(7)	(6)	(5)	1)	1)	1)		2(1)		
COH	COH Capsule broken but selected for petrographic observation											
Systen	$\int C_a O_a$	$+ SiO_2$	$+ M_0 O$	+ COF	I (svnt	hetic C	- I-hearin	a chry	sotile)			
System	i CuO	+ 5102	+ MgO	+ 001		nene Ci	i-Deurin	g chi y.	some)			
COH	58.1	33.8(20.4	0.22	0(1	62.0(37.6(0.4(0(2)	0.37	0.853(4)	0.89(3)
201	0	1)	6(9)	(6)	XY	2)	2)	1)		7(2)		
COH	39.8	14.4(24.0(0.1	0(3	37.4(62.2(0.4(0(7)	0.62	1.000(9)	1.06(7)
146	3	3)	2)	2))	7)	6)	4)		5(7)		
COH	6.72	1.34(2.70(0.03	0.0	32.9(66.4(0.7(0(8)	0.66	—	
147		3)	2)	(2)	(3)	7)	6)	5)		8(7)		
System $CaO + SiO_2 + MgO + COH$ (natural Fe–Al-bearing antigorite)												
COH	59.3	38.0	11.2	0.20	1.9	73.9(21.9(0.40	3.8(0.22	0.491(3)	0.58(2)
119	6	2(5)	9(6)	(5)	(5)	1)	1)	(9)	9)	9(1)		
COH	85.7	57.9	17.4	0.16	3.4	73.3	22.1	0.20	4.3(0.23	0.759(3)	0.91(3)
126	7	2(6)	5(7)	(5)	(5)	6(8)	1(9)	(7)	6)	2(1)		
$^{I}X_{Cat} = Cal/(Cal \pm Q \pm Ctl \pm Atg)_{molar}; ^{II}X_{CH4} = CH_4/(CH_4 + H_2O)_{molar}; ^{III}Molar ratio between the generated$												

CH₄ and starting calcite; ^{IV}Molar ratio between the generated total C-bearing species (including CH₄, CO₂, and CO) and starting calcite.

FIGURE CAPTIONS

Fig. 1. (a–c) Schematic illustration of the double capsule system. The inner $Au_{60}Pd_{40}$ capsule contains starting materials, including (a) calcite + water, (b) layered calcite + quartz + water, and (c) layered calcite + serpentine (synthetic Chbearing chrysotile and natural Fe–Al-bearing antigorite) + water. The outer Au capsule contains the inner capsule and the IW + H₂O buffering assemblage. Due to H₂ permeability of the Au₆₀Pd₄₀ alloy, *f*H₂ conditions are homogeneous in the inner and outer capsules. (d) Back-scattered electron image showing the preservation of iron and wüstite in the outer capsule after quenching. (e) The log fO_2-P diagram calculated at a fixed temperature of 550 °C for a variety of oxygen buffers. Mineral abbreviations in this study follow Whitney & Evans (2010).

Fig. 2. Molar ratios between the generated CH_4 and staring calcite (CH_4/Cal_{molar}) in the experiments, with run numbers denoted. The larger symbol sizes represent the longer run durations (24 h, 72 h, 96 h, and 240 h). Hollow and solid symbols represent experiments at 1 GPa and 2 GPa, respectively.

Fig. 3. Solid products in runs (a–c) COH193 and (d–f) COH194 (P = 1 GPa, T = 550 °C). Portlandite crystals grow at the expense of calcite grains, with the portlandite selvage width in run COH194 larger than that in run COH193.

Fig. 4. Solid products in run COH121 (P = 2 GPa, T = 550 °C). (a) Back-scattered electron image and (b) compositional X-ray map showing the layered distribution of portlandite, larnite, and wollastonite between aragonite and quartz.

Fig. 5. Solid products in runs (a–c) COH146 (P = 1 GPa, T = 550 °C) and (d–f) COH147 (P = 2 GPa, T = 550 °C). (a & b) Growth of portlandite and larnite (in

association with brucite) by replacing calcite, with merwinite inclusions visible in larnite. (c) Relatively even distribution of portlandite, larnite, and brucite. (d–f) Mineral assemblage of portlandite, larnite, and brucite, with the latter two commonly showing an intergrown texture.

Fig. 6. Solid products in runs (a–c) COH119 (P = 1 GPa, T = 550 °C) and (d & e) COH126 (P = 2 GPa, T = 550 °C). (a) Cross section of the capsule showing solid products in the inner Au₆₀Pd₄₀ capsule and the IW buffer in the outer Au capsule. Starting calcite is partly replaced by the newly formed phases including portlandite. (b & c) Enlargement of boxes in (a) showing the occurrence of larnite, brucite, and monticellite (enclosing small amounts of forsterite-rich olivine) as well as chlorite. (d) Portlandite having aragonite inclusions and coexisting with larnite. (e) Intergrowths of larnite and brucite, with merwinite and vesuvianite visible.

Fig. 7. Phase stabilities under variable fO_2 and fH_2 conditions in the (a & b) CaO + COH, (c & d) CaO + SiO₂ + COH (with the CaCO₃ and SiO₂ molar ratio of 3:2), and (e & f) CaO + SiO₂ + MgO + COH (with the CaCO₃ and Mg₃Si₂O₅(OH)₄ molar ratio of 9:1) systems both at 1 and 2 GPa at 550 °C. Orange dashed lines show log fO_2 values of the HM, FMQ, IW, and QIF buffers. The red cross constrains fO_2 and fH_2 values in the outer capsule while fO_2 conditions in the inner capsule are slightly lower than fO_2^{TW} (see text for details).

Fig. 8. Evolution of (a) minerals (including calcite reactant and portlandite product, as well as calcite consumed in the reaction), (b & c) dissolved elements and species in the fluids, and (d) fO_2 and fH_2 conditions through interactions between reduced fluids and calcite in the CaO + COH system at 1 GPa and 550 °C for the F/R ratio

of 2. Each unit of the reaction progress variable corresponds to destruction of 1.0 mol of calcite reactant and mixing with the EQ3 fluids containing 1.0 kg of H_2O .

Fig. 9. Reaction rate constants retrieved on the basis of molar ratios between the generated CH_4 and starting calcite (CH_4/Cal_{molar}) and run durations at 1 GPa and 550 °C. Due to the limited experimental data, rate constants for reactions starting with calcite + quartz + water and calcite + natural antigorite + water were roughly constrained.

Fig. 10. Results of representative experiments on HP aqueous reduction of carbonate minerals or organic matter at variable fO_2 under subduction zone conditions (data from Sharma *et al.*, 2009; Lazar *et al.*, 2014; Li, 2017; Mukhina *et al.*, 2017; and this study). For comparison, $P-T-fO_2$ conditions for abiotic CH₄ generation through HP carbonate reduction in natural samples from the Italian Western Alps (Vitale Brovarone *et al.*, 2017; Giuntoli *et al.*, 2020) and the Chinese southwestern Tianshan (Tao *et al.*, 2018) are shown. Grey and black colors filled in symbols represent the presence of CH₄ and graphite, respectively. The purple and light purple areas display the modelled prograde P-T paths of subduction zones at the slab interface and slab Moho, respectively (Syracuse *et al.*, 2010).

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Fig. 10.

