

Abiotic methane formation during experimental serpentinization of olivine

Thomas M. McCollom^{a,1}

^aLaboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309

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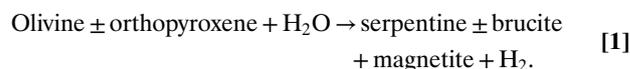
Fluids circulating through actively serpentinizing systems are often highly enriched in methane (CH₄). In many cases, the CH₄ in these fluids is thought to derive from abiotic reduction of inorganic carbon, but the conditions under which this process can occur in natural systems remain unclear. In recent years, several studies have reported abiotic formation of CH₄ during experimental serpentinization of olivine at temperatures at or below 200 °C. However, these results seem to contradict studies conducted at higher temperatures (300 °C to 400 °C), where substantial kinetic barriers to CH₄ synthesis have been observed. Here, the potential for abiotic formation of CH₄ from dissolved inorganic carbon during olivine serpentinization is reevaluated in a series of laboratory experiments conducted at 200 °C to 320 °C. A ¹³C-labeled inorganic carbon source was used to unambiguously determine the origin of CH₄ generated in the experiments. Consistent with previous high-temperature studies, the results indicate that abiotic formation of CH₄ from reduction of dissolved inorganic carbon during the experiments is extremely limited, with nearly all of the observed CH₄ derived from background sources. The results indicate that the potential for abiotic synthesis of CH₄ in low-temperature serpentinizing environments may be much more limited than some recent studies have suggested. However, more extensive production of CH₄ was observed in one experiment performed under conditions that allowed an H₂-rich vapor phase to form, suggesting that shallow serpentinization environments where a separate gas phase is present may be more favorable for abiotic synthesis of CH₄.

serpentinization | abiotic methane | hydrothermal systems

Fluids discharged from actively serpentinizing ultramafic rocks in both subaerial and submarine settings are often enriched in methane (CH₄) as well as molecular hydrogen (H₂) (1–5). The CH₄ in these fluids can provide chemical energy to support chemosynthetic microbial communities (6, 7), and metabolic pathways linked to CH₄ in serpentinizing environments may have been among the first to evolve on Earth (8–10). Serpentinization has also been proposed as a possible source for the transient CH₄ that has been reported in the atmosphere of Mars (11, 12).

The origin of the elevated CH₄ found in many serpentinizing fluids has been the subject of considerable scientific study over the last several decades, with possible contributors including microbial methanogenesis, thermal decomposition of larger organic compounds, and abiotic synthesis from reduction of inorganic carbon in the subsurface (reviewed in ref. 13). Although laboratory experiments can help to constrain the contribution of abiotic synthesis to fluxes of CH₄ in serpentinites, published studies have reported some seemingly conflicting results with regard to the potential for reduction of inorganic carbon to CH₄ during serpentinization (14, 15). Experimental studies performed at high temperatures (300 °C and above) have shown that there exist strong kinetic barriers to abiotic CH₄ synthesis unless certain catalytic minerals, such as NiFe alloys, are present (16–21). Conversely, several recent studies have reported abiotic synthesis of CH₄ during reaction of olivine with aqueous solutions at much lower temperatures (25 °C to 200 °C) (22–25), although the kinetic barriers might be expected to preclude abiotic CH₄ synthesis at these conditions.

The process of serpentinization can be summarized by the general reaction



In this process, oxidation of ferrous Fe (Fe^{II}) from the reactant minerals to ferric Fe (Fe^{III}) in the products is coupled to reduction of water to produce H₂ (26). Reaction of the H₂ with dissolved inorganic carbon can then lead to formation of CH₄, which can be expressed by the reaction



The first experimental study to attempt a detailed examination of the abiotic production of CH₄ and other hydrocarbons during serpentinization was that of Berndt et al. (27). These authors reported production of CH₄ along with small amounts of ethane (C₂H₆) and propane (C₃H₈) during reaction of olivine with water at 300 °C. Formation of the CH₄ and other hydrocarbons was attributed to reduction of dissolved CO₂ by H₂ catalyzed by magnetite generated during serpentinization (Reaction 1). However, when this experiment was replicated using a ¹³C-labeled inorganic carbon source to trace the origin of organic compounds (i.e., H¹³CO₃[−]), it was found that only a small fraction of the CH₄ and none of the other hydrocarbons observed during the experiment contained the ¹³C, showing that synthesis of these compounds from reduction of the inorganic carbon source was very limited under the reaction conditions (17). Instead, the methane in the experiments was composed predominantly of ¹²CH₄, indicating that it was derived from

Significance

Abiotic methane discharged from serpentinizing rocks supplies metabolic energy to chemosynthetic microbial communities and may have done so since the earliest lifeforms evolved on Earth. Several recent reports have claimed observation of abiotic formation of methane during low-temperature serpentinization of olivine-rich rocks during laboratory experiments. However, using ¹³C-labeled carbon sources, this study shows that the methane observed in such experiments is predominantly derived from background sources rather than abiotic synthesis. Conversely, more rapid production of methane is observed when an H₂-rich vapor phase is present within the reaction vessel. Overall, the results indicate that in situ abiotic synthesis may contribute less methane to near-surface serpentinites than some recent studies have suggested.

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¹To whom correspondence should be addressed. Email: mcollom@lasp.colorado.edu.

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background sources of reduced carbon present in the olivine or other reaction materials. Several subsequent experimental studies confirmed that abiotic reduction of dissolved CO_2 to CH_4 is sluggish at temperatures as low as 300 °C, even in the presence of highly elevated H_2 concentrations, except when NiFe alloy was present (16, 18–21). Additional experiments with ^{13}C -labeled inorganic carbon compounds also confirmed that background sources are a ubiquitous contributor to CH_4 in experimental fluid–rock studies using olivine or other minerals, with abundance that often far exceeds that of bona fide synthesis products (18, 19, 28).

Although these studies provided substantial evidence for kinetic inhibition to abiotic CH_4 synthesis at elevated temperatures, several other studies in recent years have reported abiotic production during experimental alteration of olivine at much lower temperatures of 25 °C to 200 °C (22–25). In each of these experiments, olivine was heated with aqueous fluids, and production of micromolar concentrations of CH_4 was observed. The CH_4 generated in these experiments was interpreted to come from abiotic reduction of inorganic carbon. However, because ^{13}C labeling or other methods to identify the source of the CH_4 were not used, the actual origin of this compound is uncertain.

To better understand the potential for abiotic CH_4 synthesis during serpentinization of olivine-rich ultramafic rocks, production of CH_4 was monitored in a series of hydrothermal experiments reacting olivine with inorganic carbon-bearing aqueous solutions (Table 1). Results reported here focus on carbon reduction and CH_4 synthesis during these experiments, whereas a detailed analysis of other products and reaction rates has been reported elsewhere (29). In all of the experiments, a ^{13}C -labeled compound was used as the inorganic carbon source (in the form of $\text{NaH}^{13}\text{CO}_3$) to trace the conversion of inorganic carbon to CH_4 . That is, production of $^{13}\text{CH}_4$ during the experiments would provide unambiguous evidence that synthesis of CH_4 from reduction of inorganic carbon occurred during the experiments, whereas production of $^{12}\text{CH}_4$ would indicate that the methane derived from a background source of reduced carbon. The experiments were conducted over a temperature range of 200 °C to 320 °C. Experiments were not extended to lower temperatures, because the rates of serpentinization were found to be too slow below 200 °C to be readily observable on laboratory timescales (29, 30).

Most experiments were conducted with olivine as the mineral reactant, although one experiment also included orthopyroxene (OPX; OLIVOPX230). To focus on reactions involving dissolved compounds, most experiments were conducted at a pressure of 35 MPa. However, one experiment (OLIV300_sat2) was conducted at conditions intended to allow formation of a separate H_2 -rich vapor phase in the reaction cell to test whether vapor-phase reactions would allow more efficient synthesis of CH_4 . This experiment was conducted at 10 MPa, with additional H_2 injected into the reaction cell at the outset to encourage formation of a separate H_2 -rich vapor phase (31).

Results

Solid reaction products of all experiments included chrysotile, Fe-bearing brucite, magnetite, and small amounts of carbonates (magnesite and dolomite) (29). In experiment OLIVOPX230, the products also included trace amounts of an Ni-Fe phase (presumably awaruite or other NiFe alloy) and native Pt (Fig. S1). In addition to these reaction products, the experiments all contained substantial amounts of relict olivine, indicating that the serpentinization reactions went only partially to completion, despite prolonged reaction times lasting up to 13 mo. Estimates of the extent of reaction ranged from 2.7 to 48% (Table 1). Although the reactants for experiment OLIVOPX230 initially contained ~14 wt % OPX, only olivine persisted at the end of the experiment. For reasons that are not yet clear, addition of OPX to the experimental charge in OLIVOPX230 led to much faster reaction rates for both olivine and OPX, resulting in a much greater extent of reaction and higher H_2 concentrations (Table 1). The H_2 concentration in this experiment exceeded the amount required to stabilize awaruite according to recent experimental studies (32), consistent with the observed formation of NiFe alloy. The olivine used in the experiments contains 0.30 wt % Ni, providing a source for this element in the alloy.

Each of the experiments exhibited steady increases in H_2 during heating as a result of the serpentinization reaction (Fig. 1 A and B). Concentrations of dissolved H_2 reached values exceeding 2.8 mmol kg^{-1} in all of the experiments and attained especially high levels in experiments OLIVOPX230 (61 mmol kg^{-1}) and OLIV300_sat2 (194 mmol kg^{-1}) (Table 1). The latter experiment was designed to produce a separate H_2 -rich vapor phase within the reaction vessel during heating. The H_2 concentration in this experiment rose to 180 mmol kg^{-1} within the first 2,012 h of reaction, and then remained essentially constant within analytical error over the following 1,873 h, although additional H_2 would have been generated with continued reaction. The observed concentration is consistent with saturation of liquid water with H_2 at the experimental temperature and pressure (Fig. S2) (31), suggesting that the nearly constant concentration can be attributed to the fluid maintaining equilibrium with an H_2 -rich vapor phase. This phase would probably have been present as a small bubble (or bubbles) in the reaction cell. It is likely that some CO_2 and CH_4 would have partitioned into the vapor phase as well. However, although the evidence indicates a separate H_2 -rich vapor phase formed within the reaction cell, limitations in the experimental design did not allow this phase to be sampled to confirm its presence or determine its composition.

Levels of dissolved CH_4 also increased steadily during each of the experiments, although concentrations of this compound remained several orders of magnitude lower than those of H_2 (Fig. 1 C and D and Table 1). Total dissolved CO_2 [$\Sigma\text{CO}_2 = \text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$] decreased gradually during each of the experiments, except the one performed at 320 °C (OLIV320),

Table 1. Summary of experimental parameters and final fluid compositions

Experiment	Temperature (°C)	Duration (h)	Initial fluid (g)	Initial minerals	Reaction (%)	Final H_2 (m)	Final ΣCO_2 (m)	Final CH_4 (μ)	$^{13}\text{CH}_4$ (%)
OLIV200_fine	200	1,823	36	17 g olivine*	9.3	2.9	9.6	15	1
OLIV230	230	8,183	42	25 g olivine [†]	4.8	5.8	6.0	5.5	1
OLIV300	300	2,683	42	20 g olivine [†]	2.8	11	12.5	25	1
OLIV300_sat2	300	3,885	42	31 g olivine [†]	21	194	11.0	98	53
OLIV320	320	2,087	38	15 g olivine [†]	2.7	2.6	18.1	270	6
OLIVOPX230	230	9,287	44	21 g olivine [†] + 3.5 g OPX [†]	48	61	2.8	25	1

Concentrations are in millimoles kilogram⁻¹ (m) or micromoles kilogram⁻¹ (μ).

*Grain size = 38–53 μm .

[†]Grain size = 53–212 μm .

[‡]Olivine used in this experiment was finely powdered, but grain size distribution was not determined.

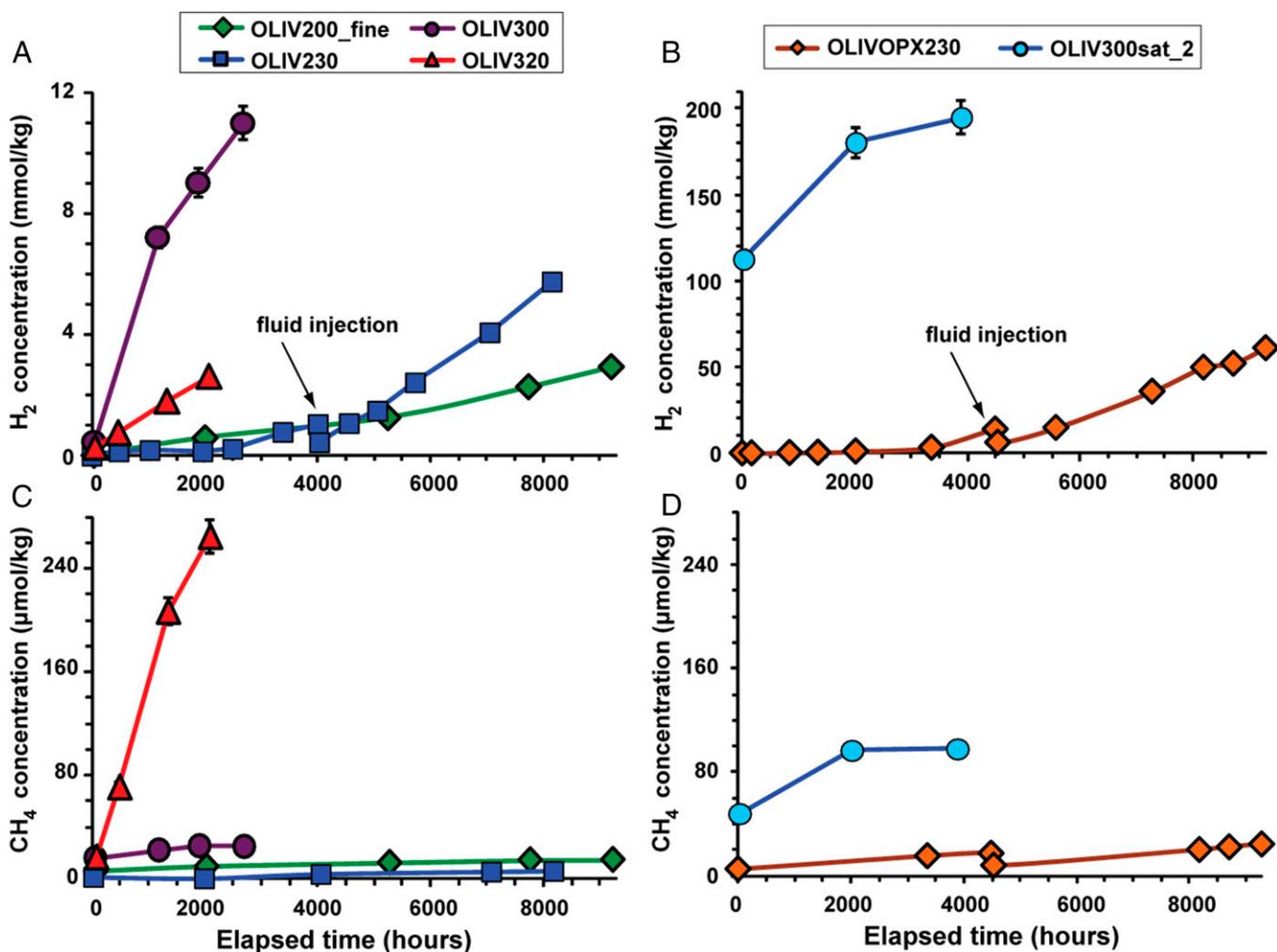


Fig. 1. Measured concentrations of dissolved volatiles during serpentinization experiments. (A and B) Dissolved H_2 . (C and D) Dissolved CH_4 . For experiments OLIV230 and OLIVOPX230, additional fluid was injected into the reaction cells during heating to replace fluid removed for chemical analysis, resulting in a transient decrease in dissolved concentrations. Except where shown, estimated analytical errors are smaller than the size of the symbols. Methane was not measured at all sample points to conserve fluid. The measured concentrations are provided in Table S1, with additional data on fluids compositions given in ref. 29.

but in all cases, concentrations remained at 2.8 mmol kg^{-1} or higher at the end of the experiments (Table S1). The decrease in ΣCO_2 during heating is predominantly attributable to the formation of carbonate minerals, which were found dispersed among the product minerals in the experiments (29). Concentrations of C_{2+} hydrocarbons were near or below detection limits in all samples ($<0.01 \text{ } \mu\text{mol kg}^{-1}$).

Although CH_4 increased during heating in all experiments, in most cases, it remained at fairly low concentrations ($\leq 25 \text{ } \mu\text{mol kg}^{-1}$). Furthermore, the CH_4 produced in most experiments was composed predominantly of $^{12}CH_4$ (Fig. 2 and Table 1), indicating little or no contribution from the labeled inorganic carbon source ($NaH^{13}CO_3$) added to the experiments. Consequently, the CH_4 observed in these experiments must have been derived entirely from background sources of reduced carbon contained in the reaction materials rather than reduction of dissolved inorganic carbon.

Substantially higher levels of CH_4 ($270 \text{ } \mu\text{mol kg}^{-1}$) were generated in the experiment performed at $320 \text{ } ^\circ\text{C}$ (OLIV320) (Fig. 1C). In addition, the methane in this experiment contained about 6 mol % $^{13}CH_4$ (Fig. 2), indicating a minor contribution from reduction of dissolved inorganic carbon. This reduction can account for $\sim 16 \text{ } \mu\text{mol kg}^{-1}$ of the total dissolved CH_4 , indicating

that the higher temperature also led to a larger contribution of $^{12}CH_4$ from background sources ($\sim 250 \text{ } \mu\text{mol kg}^{-1}$) than occurred at lower temperatures.

Relatively high levels of dissolved CH_4 were also observed in experiment OLIV300_sat2 ($98 \text{ } \mu\text{mol kg}^{-1}$) (Fig. 1D). Because some CH_4 would have partitioned into the vapor phase that may have been present in this experiment, the total amount of CH_4 generated could be even higher than indicated by the dissolved concentration. The methane produced in OLIV300_sat2 also contained 53 mol % $^{13}CH_4$ (Fig. 2), indicating that $\sim 50 \text{ } \mu\text{mol kg}^{-1}$ of the dissolved CH_4 was formed by reduction of the added inorganic carbon source. Again, if some CH_4 partitioned into a vapor phase, the total amount of $^{13}CH_4$ formed from reduction of inorganic carbon would have been even higher than the dissolved concentration indicates.

Discussion

Steady increases in the abundance of dissolved CH_4 and H_2 were observed in all of the serpentinization experiments performed for this study (Fig. 1). In the absence of the isotope measurements, it might seem reasonable to infer that the CH_4 was produced by abiotic reduction of inorganic carbon through reaction with H_2 generated from serpentinization (Reactions 1 and 2). However,

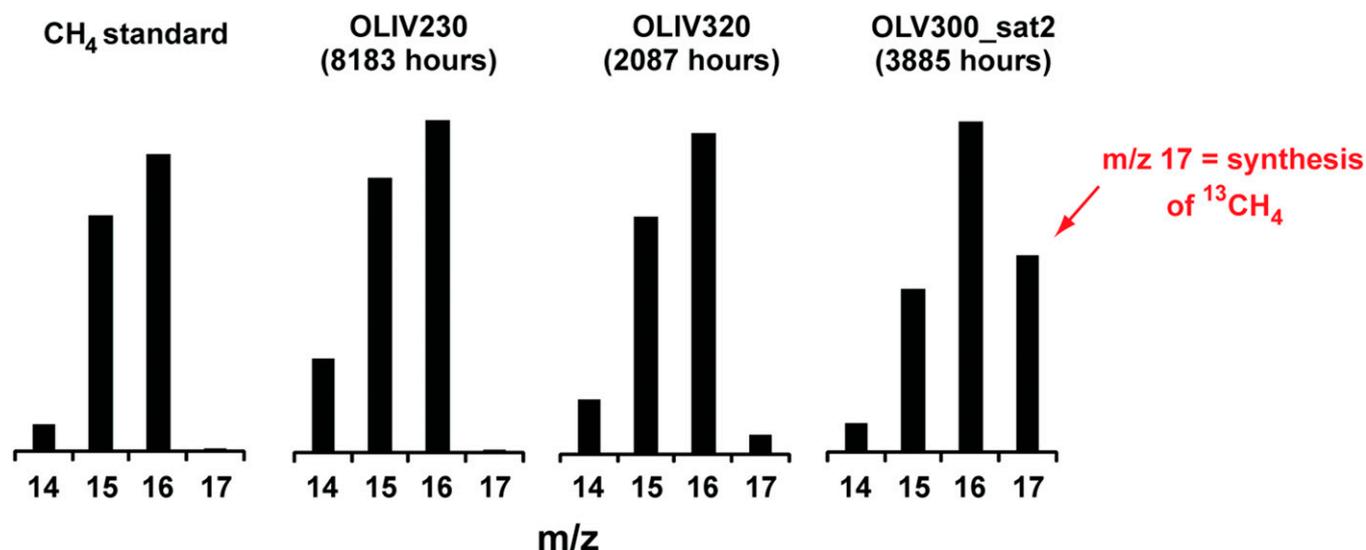


Fig. 2. Representative mass fragmentograms for CH₄ generated during serpentinization experiments. Also shown for reference is analysis of a methane gas standard. For the reference standard, prominent peaks occur at *m/z* 15 and 16, corresponding to *m/z* values for the ions ¹²CH₃⁺ and ¹²CH₄⁺, respectively. The small peak at *m/z* 17 in the standard reflects a small amount of ¹³CH₄⁺ (~1 mol % at natural abundance). Higher amounts of *m/z* 17 in some experiment samples indicate contributions from ¹³CH₄ formed through reduction of dissolved inorganic carbon [¹³CO_{2(aq)} or H¹³CO₃⁻] during the experiments.

the isotopic measurements clearly show that in situ carbon reduction was not the predominant source of the CH₄ in all but one of the experiments. Instead, the results indicate that the most of observed CH₄ was ¹²CH₄ derived from background sources. This ¹²CH₄ must have originated from carbon that was already present in a reduced form at the start of the experiments, because very little or no reduction of inorganic carbon was observed. Possible contributors to this background ¹²CH₄ include volatiles released from fluid inclusions, reaction of reduced carbon present on crack surfaces within the crystals (33), or thermal breakdown of contaminating organic compounds inadvertently included in the reaction materials. However, the actual source remains to be determined.

It is worth emphasizing that there was a strong thermodynamic drive for conversion of the dissolved inorganic carbon to CH₄ in each of the experiments, with the possible exception of OLIV320. That is, thermodynamic calculations indicate that, at the elevated H₂ concentrations of the experiments, essentially all of the dissolved carbon should have been converted to CH₄ at equilibrium (Fig. S3). The persistence of a large fraction of carbon as ΣCO₂ is attributable to the strong kinetic inhibitions to carbon reduction in aqueous environments at temperatures below about 400 °C (17–21).

The results reported here are consistent with previous laboratory studies performed with serpentinite-related minerals at temperatures ≥300 °C that show both limited abiotic synthesis of CH₄ and relatively high levels of CH₄ from background sources (17–21, 28). However, the results disagree with other recent reports, where the CH₄ produced during experimental reaction of olivine with aqueous solutions has been interpreted to be predominantly derived from abiotic reduction of dissolved inorganic carbon (22–25). For example, Oze and coworkers (24, 25) investigated formation of CH₄ in a series of laboratory experiments in which olivine was reacted with aqueous solutions at 200 °C. These experiments were performed using methods very similar to those of this study, except that the reaction vessel was periodically rotated during heating. After heating for 22–36 d, those authors observed dissolved H₂ concentrations between 4.8 and 6.3 mmol kg⁻¹ and CH₄ concentrations between 44 and 120 μmol kg⁻¹ depending on reaction parameters. The CH₄ observed in their experiments was interpreted to be produced by catalyzed

reduction of dissolved inorganic carbon via Fischer–Tropsch-type reactions, with magnetite formed during serpentinization serving as the catalyst (25).

The levels of dissolved H₂ and CH₄ observed in the study by Oze et al. (25) are comparable with those occurring in our experiments performed at similar temperatures (200 °C to 230 °C) (Table 1). However, isotopic labeling indicated that the CH₄ in our experiments was not derived from reduction of dissolved inorganic carbon but instead, was derived entirely from background sources (i.e., composed of 99 mol % ¹²CH₄). Although magnetite was a widespread reaction product in the experiments presented here (0.25–1.6 wt % of solids after reaction) (29), the lack of ¹³CH₄ in the products indicates that it was not capable of catalyzing synthesis of this compound from reduction of dissolved inorganic carbon under the experimental conditions. Consequently, the capacity for magnetite to catalyze abiotic CH₄ synthesis in experimental and natural systems seems to be substantially less than inferred by Oze et al. (25), at least for dissolved substrates.

Results of this study as well as those of other studies using ¹³C-labeled carbon sources (17–19, 28) strongly suggest that the CH₄ observed in the laboratory experiments of Jones et al. (24) and Oze et al. (25) was derived predominantly from background sources rather than Fischer–Tropsch-type reduction of inorganic carbon as those authors inferred. In their experiments, there was no use of ¹³C-labeled compounds or other methods to rigorously evaluate the source of carbon in the CH₄ generated during heating. Although the levels of dissolved CH₄ observed in the studies of Jones et al. (24) and Oze et al. (25) were somewhat higher than those in the present experiments (44–120 vs. 5.5–25 μmol kg⁻¹ for experiments performed at 200 °C to 230 °C) (Table 1), the lower levels of background sources observed here are likely attributable to extensive efforts to purify the mineral reactants and avoid introduction of potential organic contaminants into the reaction materials (29) as well as more extensive olivine reaction in the other studies. Oze et al. (34) argue that carbonate undersaturation led to higher generation rates of H₂ and abiotic CH₄ in their experiments, but there is no logical reason to expect that undersaturation would enhance the rate of carbon reduction.

Based on the presumed abiotic synthesis of CH₄ in laboratory serpentinization experiments performed by themselves and others,

Oze et al. (25) proposed that H_2/CH_4 ratios could be used to infer the relative contributions of biotic and abiotic methane sources in hydrothermal fluids discharged from serpentinites on Earth and elsewhere. Notably, in their analysis, Oze et al. (25) assumed that all of the CH_4 observed in prior serpentinization experiments was derived from magnetite-catalyzed reduction of inorganic carbon, even in those cases where ^{13}C labeling had clearly shown that only a small fraction of the observed CH_4 was derived from this source (17, 19). When the results reported here and elsewhere are taken into consideration, which show that the CH_4 in laboratory experiments is predominantly derived from background sources rather than carbon reduction, the use of experimentally determined H_2/CH_4 ratios to place constraints on the source of CH_4 in hydrothermal fluids appears to be invalid.

The results reported here also seem to disagree with recent claims of abiotic production of CH_4 in olivine–water interaction experiments conducted at lower temperatures (25 °C to 70 °C) (22, 23). In these studies, olivine was reacted with aqueous solutions in glass bottles sealed with rubber stoppers, and CH_4 was observed to accumulate in the headspace. In one of these studies, Neubeck et al. (23) reported accumulation of CH_4 above levels observed in mineral-free blanks during 9 mo of heating at 70 °C but not at 30 °C or 50 °C. Based on the scarcity of reduced carbon sources detected in the reactant olivine, those authors suggest that the observed CH_4 was generated from carbon reduction during the experiments, perhaps catalyzed by magnetite or chromite present in trace amounts among the mineral reactants. Similarly, Okland et al. (22) reported the production of small amounts of H_2 and CH_4 above levels observed in controls during reaction of powdered olivine sand (dunite) at 25 °C over 99 d, with higher amounts of these compounds generated from partially serpentinized rocks. Although they considered contributions from background sources, these authors inferred that most of the CH_4 was derived from reduction of inorganic carbon on the surfaces of minerals during the experiments.

The results presented here and in other higher-temperature studies indicate that it is highly unlikely that the CH_4 observed in these low-temperature experiments resulted from reduction of inorganic carbon for several reasons. First, the experimental evidence indicates that there are strong kinetic inhibitions that prevent reduction of dissolved inorganic carbon to CH_4 at high temperatures, and it is extremely unlikely that these kinetic barriers would be overcome at temperatures below 100 °C when they are not overcome at 200 °C to 300 °C. Second, although known pathways for abiotic synthesis of CH_4 , such as the Fischer–Tropsch and Sabatier reactions, require molecular H_2 as a reactant (14, 15), levels of this compound in the low-temperature experiments were several orders of magnitude lower than in the higher-temperature experiments, where little or no conversion of dissolved inorganic carbon to CH_4 was observed. Consequently, if abiotic formation of CH_4 did occur in these low-temperature experiments, it would have had to involve an unrecognized reaction mechanism that does not depend on H_2 and only occurs at low temperatures (otherwise, formation of $^{13}CH_4$ by this mechanism would have been observed in the higher-temperature experiments). Third, the ubiquitous occurrence of $^{12}CH_4$ from background in labeled experiments indicates that some level of contamination of this compound will be present in all experiments involving olivine. Consequently, the most parsimonious explanation for the CH_4 observed in the low-temperature experiments is that it was generated from an unrecognized background source rather than abiotic reduction of inorganic carbon. Again, there was no use of ^{13}C labeling or other methods in these studies to confidently determine the source for the carbon in the observed CH_4 .

The only experiment in this study where substantial amounts of $^{13}CH_4$ were produced from reduction of dissolved inorganic carbon was OLIV300_sat2 (Fig. 1 and Table 1). A likely explanation for the enhanced levels of $^{13}CH_4$ production in this experiment is that the reduction of inorganic carbon took place in

the H_2 -rich vapor phase that apparently formed during the experiment. The presence of a vapor phase may have promoted the synthesis of CH_4 by allowing better contact of the reactants with catalytic mineral surfaces. Abiotic synthesis pathways, such as Fischer–Tropsch-type reactions, require that the reactants (e.g., CO_2 or CO and H_2) bond directly to the catalyst surface (17). Such bonding may occur more readily in a gas phase than in an aqueous environment, where water molecules attached to the mineral surface could interfere with the reactions. Alternatively, it is possible that the enhanced production of $^{13}CH_4$ in this experiment is attributable to the high levels of dissolved H_2 that were present, which were much higher than in the other experiments that were part of this study (Table 1). However, this alternative seems unlikely, because only very small amounts of $^{13}CH_4$ (<2 $\mu\text{mol kg}^{-1}$) were observed in another similar serpentinization experiment performed at the same temperature where the H_2 concentration attained levels ($\sim 70 \text{ mmol kg}^{-1}$) more comparable with the OLIV300_sat2 experiment (17).

If the presence of a vapor phase does account for the substantially higher production of CH_4 in OLIV300_sat2, it suggests that natural serpentinizing environments where a similar H_2 -rich vapor phase forms may be particularly favorable for abiotic synthesis of CH_4 . This situation might arise, for instance, at the serpentinization reaction front, where localized consumption of H_2O and production of H_2 (Reaction 1) can lead to saturation of the fluid and exsolution of H_2 -rich vapor bubbles. Indeed, the relatively common occurrence of the NiFe alloy awaruite in many serpentinites may be an indication that such conditions may be widespread, because formation of this mineral requires highly elevated H_2 concentrations that may approach saturation levels (32, 35). Because NiFe alloys can also catalyze the reduction of inorganic carbon to CH_4 (16), it may make these environments even more favorable for CH_4 synthesis. Nevertheless, the absence of detectable NiFe alloys in OLIV300_sat2 indicates that the presence of this mineral may not be required for CH_4 formation to occur. Although the conditions leading to saturation of H_2 are distinctly different from boiling (31), boiling of fluids in near-surface environments could also lead to vapors enriched in H_2 that could promote abiotic CH_4 synthesis.

In natural serpentinites, abiotic CH_4 has often been inferred to form by reduction of dissolved inorganic carbon as hydrothermal fluid or groundwater circulates through and interacts with ultramafic host rocks in the subsurface. The experimental results, however, indicate that abiotic reduction of dissolved inorganic carbon to CH_4 may be very limited in shallow, lower-temperature serpentinizing environments (1–5). Formation of significant amounts of abiotic CH_4 within shallow serpentinites may, therefore, require fluid residence times that are much longer than those of the experiments, the presence of awaruite or other catalytic minerals, or conditions that allow gas-phase reactions to occur.

These results seem to be consistent with a recent study concerning the origin of CH_4 in submarine hydrothermal systems by McDermott et al. (36). That study investigated the origin of CH_4 and other light hydrocarbons in fluids discharging at temperatures up to 226 °C from the Von Damm site on the Mid-Cayman Rise. Hydrothermal fluids at this site were found to contain up to 2.81 mM CH_4 . However, based on fluid compositions and carbon isotopes, McDermott et al. (36) concluded that little or none of the CH_4 was produced by reduction of dissolved inorganic carbon dissolved during circulation of seawater through the ultramafic host rocks in the subsurface, although fluid–rock interactions resulted in highly elevated H_2 concentrations (up to 18.3 mM). Instead, those authors postulated that the CH_4 was likely to be derived from fluid inclusions trapped within the rocks, where it may have formed by abiotic reactions involving magmatic vapors at temperatures above 400 °C. Results of this study support both the lack of abiotic reduction of dissolved inorganic carbon to CH_4 during circulation of seawater through the hydrothermal system

and the possibility of CH₄ synthesis at elevated temperature from magmatic volatiles.

Materials and Methods

A detailed description of the experimental procedures and products is provided in ref. 29. Briefly, experiments were conducted by reacting powdered minerals with carbon-bearing aqueous solutions at 200 °C to 320 °C (Table 1). For most experiments, powdered San Carlos olivine was used as the mineral reactant, although one experiment also included OPX from Bamble, Norway (OLIVOPX230). The minerals were sorted for purity and then, wet-sieved to obtain a uniform grain size (38–53 or 53–212 μm). Inspection of the prepared olivine reactant indicated that it contained trace amounts (<1 vol %) of several contaminating minerals, including OPX, diopside, and Mg-Al-rich spinel. The reactant solutions initially contained 485 mmol kg⁻¹ NaCl and 19.4 mmol kg⁻¹ NaH¹³CO₃.

The experiments were performed in a flexible cell reaction apparatus using a reaction cell composed of a pure Au with a titanium closure piece (29, 37). Before use, the closure piece was heated in air to form an inert TiO₂ layer. The reaction cell was connected to a valve to sample the fluid during the experiments. As the experiments progressed, aliquots of the reactant fluid were obtained intermittently to monitor production of H₂, CH₄, and other dissolved compounds. Volatile species were extracted from solution with either N₂ or He gas and quantified by GC using thermal conductivity or flame ionization detection (details are in ref. 29). At termination of the

experiments, an additional sample was obtained to assess the extent of incorporation of ¹³C into CH₄ using GC-MS (17, 19). For this analysis, the CH₄ was trapped onto a sample loop with liquid N₂ and then, released into the GC-MS. Volatile species were separated on a capillary Altech AT-Q Column with an initial oven temperature of 50 °C, maintained for 5 min, and then, raised to 240 °C at 15 °C per minute.

To ensure that reactions involved dissolved species rather than gases, most experiments were conducted at a pressure of 35 MPa. However, in an effort to determine whether the presence of a vapor phase would promote formation of CH₄, one experiment (OLIV300_sat2) was conducted using procedures intended to encourage formation of an H₂-rich vapor phase. For this experiment, generation of H₂ during the experiment was supplemented with injection of H₂ before initiation of heating to achieve an initial concentration of ~110 mmol kg⁻¹. In addition, finely powdered olivine was used in the experiment to increase the rate of serpentinization and H₂ production. Furthermore, this experiment was performed at lower pressure (10 MPa) to encourage attainment of H₂ saturation and separation of a separate vapor phase (Fig. S2).

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