Differentiating biotic from abiotic methane genesis in hydrothermally active planetary surfaces

Christopher Oze^{a,1}, L. Camille Jones^b, Jonas I. Goldsmith^c, and Robert J. Rosenbauer^d

^aDepartment of Geological Sciences, University of Canterbury, Christchurch 8140, New Zealand; ^bEnvironmental Earth System Science, Stanford University, Stanford, CA 94305; ^cDepartment of Chemistry, Bryn Mawr College, Bryn Mawr, PA 19010; and ^dUS Geological Survey, Menlo Park, CA 94025

Edited by Mark H. Thieme, University of California San Diego, La Jolla, CA, and approved May 1, 2012 (received for review March 27, 2012)

Molecular hydrogen (H₂) is derived from the hydrothermal alteration of olivine-rich planetary crust. Abiotic and biotic processes consume H₂ to produce methane (CH₄); however, the extent of either process is unknown. Here, we assess the temporal dependence and limit of abiotic CH₄ related to the presence and formation of mineral catalysts during olivine hydrolysis (i.e., serpentinization) at 200 °C and 0.03 gigapascal. Results indicate that the rate of CH₄ production increases to a maximum value related to magnetite catalyzation. By identifying the dynamics of CH₄ production, we kinetically model how the H₂ to CH₄ ratio may be used to assess the origin of CH₄ in deep subsurface serpentinization systems on Earth and Mars. Based on our model and available field data, low H₂/CH₄ ratios (less than approximately 40) indicate that life is likely present and active.

kinetics | molecular hydrogen | Fischer–Tropsch type reactions | methanogenesis

Olivine hydrolysis (i.e., serpentinization) is a major pathway related to the near-surface synthesis of molecular hydrogen (H₂) on Earth, Mars, and, potentially, other planets and satellites (1–4). Molecular hydrogen from serpentinization can chemically reduce carbon (e.g., HCO₃[−], HCOOH, CO, CO₂) to form CH₄ or can be converted to CH₄ via microbial processes (i.e., methanogenesis) (1, 3, 5–12). Although CH₄ formation is thermodynamically favorable over a range of pressure (P) and temperature (T) (13, 14), CH₄ production via Fischer–Tropsch type (FTT) reactions is slow without the aid of mineral catalysts (3, 9, 15, 16). To understand the limits of abiotic CH₄ production, it is imperative to assess the role of mineral catalysts, both those initially present in the system and those formed during the process of serpentinization.

Chromite (FeCr₂O₄), a primary mineral common in serpentinization systems, has been shown to enhance FTT synthesis reactions (17). Additionally, secondary minerals such as magnetite (Fe₃O₄) and/or awaruite (Ni₃Fe) are produced during olivine hydrolysis, providing increased opportunities for FTT catalysis (13, 15, 18–21). Here, we evaluate the rate of abiotic CH₄ production for systems catalyzed both by chromite and secondary minerals (magnetite and awaruite) in experimental systems undergoing serpentinization at 200 °C and 0.03 gigapascal (GPa), conditions similar to hydrothermally altered peridotite in mid-ocean ridge environments on Earth or at approximately 5 km depth in the Martian subsurface. By measuring H₂ and CH₄ formed during olivine hydrolysis, mineral-catalyzed CH₄ production can be differentiated from biogenic CH₄ production through a consideration of the H₂–CH₄ kinetic balance.

Experimental Procedures

Serpentinization experiments were carried out in the Water–Rock Interaction Laboratory (US Geological Survey, Menlo Park, CA) using the parameters listed in Table 1. Olivine [(Fe_{0.12}Mg_{0.88})₂SiO₄ or Fo₈₈ with 2,510 mg kg^{−1} of Ni], chromite [(Fe_{0.24}Mg_{0.76})(Cr_{0.59}Al_{0.41})₂O₄], and synthetic seawater were prepared and characterized using methods outlined in *Materials and Methods* and by Jones et al. (22). The amount of chromite

Table 1. Reactants and experimental parameters

Variable	Exp. 1	Exp. 2
Olivine (Fo ₈₈)	52.0 g	67.7 g
Chromite	—	0.354 g
Evolved seawater	132 g	175 g
Water:rock	2.5:1	2.5:1
Pressure	0.030 ± 0.002 GPa	0.030 ± 0.004 GPa
Temperature	200 ± 0.8 °C	200 ± 1.1 °C

(approximately 1 wt.%) added was analogous to the typical content of oceanic peridotites (23); however, the surface area of the chromite was greater than in natural systems because of moderate powdering. Despite best practices to control and account for carbon, olivine and chromite [$<0.04\%$ total/organic carbon (LECO)] and N₂-purged synthetic seawater provided residual sources of carbon for CH₄ generation that, in total, were below carbonate saturation [see McCollom and Seewald (13) and Jones et al. (22) for discussions of carbon sources, thermodynamic routes of CH₄ formation, and the impact of carbon species in serpentinization systems]. Samples of the experimental fluid were periodically withdrawn and analyzed for pH, H₂, and CH₄. For both experiments, the pH values increased from 6 to 11 during the first 200 h and then remained constant.

Results and Discussion

The quantity of H₂ and CH₄ as well as the H₂/CH₄ ratios are shown as a function of time (h) in Fig. 1 for Exps. 1 (no chromite) and 2 (chromite added). The duration of Exp. 1 was 525 h, while Exp. 2 ran for 861 h. In Exp. 1, H₂ and CH₄ measurements were not collected after 525 h because of a leak in the autoclave. Rates of H₂ and CH₄ production are calculated via least square linear regression and are given with their respective standard deviations in Fig. 1. Hydrogen production rates in Exps. 1 and 2 are 11 ± 2 and $9 \pm 1 \mu\text{mol kg}^{-1} \text{h}^{-1}$, respectively. Methane production rates in both experiments are similar for the first 500 h: 0.09 ± 0.02 (Exp. 1) and 0.08 ± 0.01 (Exp. 2) $\mu\text{mol kg}^{-1} \text{h}^{-1}$. While Exp. 1 gas measurements were terminated at 525 h because of a slow gas leak, the rate of CH₄ production in Exp. 2 appears to increase to $0.19 \pm 0.07 \mu\text{mol kg}^{-1} \text{h}^{-1}$ after 500 h. Assuming the CH₄ production rate was constant, the overall average rate of CH₄ production for Exp. 2 is $0.15 \pm 0.02 \mu\text{mol kg}^{-1} \text{h}^{-1}$.

The evolution of the ratio of total H₂ to total CH₄ (Fig. 1) shows the relationship between H₂ generated through olivine hydrolysis and CH₄ generated through carbon reduction. If the rates of each process change during the course of the experiment,

Author contributions: C.O. designed research; C.O., L.C.J., J.I.G., and R.J.R. performed research; C.O., L.C.J., J.I.G., and R.J.R. analyzed data; and C.O., L.C.J., J.I.G., and R.J.R. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹To whom correspondence should be addressed. E-mail: christopher.oze@canterbury.ac.nz.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1205223109/-DCSupplemental.

Fig. 4. Our model is shown for serpentinization-fueled H_2 production and CH_4 formation utilizing H_2/CH_4 ratios, data points, and rates from Fig. 1 (see *Materials and Methods*) and the framework presented in Fig. 3. Data from other studies demonstrate that abiotic serpentinization systems (i.e., laboratory experiments) have H_2/CH_4 ratios equal to or greater than approximately 40 and serpentinization systems where life is present have H_2/CH_4 ratios less than approximately 40.

Materials and Methods

Olivine, chromite, and synthetic seawater were prepared and characterized as shown in Jones et al. (22). The average composition of olivine was determined to be $(\text{Fe}_{0.12}\text{Mg}_{0.88})_2\text{SiO}_4$ or $\text{Fe}_{0.88}$ based on electron microprobe microanalysis on an automated JEOL 733A electron microprobe (15-kV accelerating potential and a 15-nA beam current). Additionally, major and minor element chemistry for olivine and chromite were obtained by completely dissolving the minerals using a mixture of hot, concentrated nitric, perchloric, and hydrofluoric acids. Elemental concentrations such as Ni (as shown in *Experimental Procedures*) were measured in the supernatant using inductively coupled atomic emission spectroscopy. Synthetic seawater was prepared with reagent-grade KCl (0.0747 wt. %), CaCl_2 (0.205 wt. %), and NaCl (2.76 wt. %) in deionized water to approximate the typical "evolved" seawater chemistry in mid-ocean ridge and forearc serpentinization sites (34). Residual solids following hydrothermal alteration were evaluated using: (i) FEI 600 Quanta field effect gun (FEG) scanning electron microscope with EDS and/or a Hitachi S-4700 field-emission scanning electron microscope (FESEM) with EDS, and (ii) XRD with Bragg-Brentano/monochromator capabilities using a Rigaku Ultima IV operating at 40 kV and 40 mA (using $\text{CuK}\alpha$ radiation). X-ray diffraction patterns were collected between 2θ values of 5–90° and at a scan speed

of $0.01^{\circ} \text{ min}^{-1}$. The software package JADE (with Rietveld refinement capabilities) was used for XRD data analysis and mineral identification.

The model that was used to simulate the H_2/CH_4 ratios was constructed using Microsoft Excel ([Dataset S1](#)). Data points were calculated every 10 h for a total of 2,000 h, based on the various rates of H_2 and CH_4 generation observed. For all models presented in Fig. 4, the rate of H_2 generation was assumed to increase rapidly from $0.1 \mu\text{mol kg}^{-1} \text{hr}^{-1}$ to $10 \mu\text{mol kg}^{-1} \text{h}^{-1}$ and then to remain constant at $10 \mu\text{mol kg}^{-1} \text{h}^{-1}$ for the duration of the experiment. For all models presented in Fig. 4, the rate of CH_4 production was assumed to increase from $0.02 \mu\text{mol kg}^{-1} \text{h}^{-1}$ to $0.08 \mu\text{mol kg}^{-1} \text{h}^{-1}$ during the first 250 h of the experiment. The rate of CH_4 production was held constant at $0.08 \mu\text{mol kg}^{-1} \text{h}^{-1}$ for 300 h and was then increased after 550 h to a rate that persisted for the remainder of the experiment. In order to simulate different H_2/CH_4 ratios, only this final rate of CH_4 production was varied.

ACKNOWLEDGMENTS. We thank Bill Evans and John Fitzpatrick for analytical expertise and support, Peter Swarzenski and Renee Takesue for their reviews at the US Geological Survey, and two anonymous reviewers for their constructive and thoughtful comments.

1. Kelley DS, et al. (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30°N. *Nature* 412:145–149.
2. Sleep NH, et al. (2004) H₂-rich fluids from serpentinization: Geochemical and biotic implications. *Proc Natl Acad Sci USA* 101:12818–12823.
3. Charlou JL, et al. (2010) High production and fluxes of H₂ and CH₄ and evidence of abiotic hydrocarbon synthesis by serpentinization in ultramafic-hosted hydrothermal systems in the Mid-Atlantic Ridge. *Diversity of Hydrothermal Systems on Slow Spreading Ocean Ridges*, Geophysical Monograph, eds PA Rona, CW Devey, J Dymant, and BJ Murton pp:265–296.
4. Oze C, Sharma M (2007) Serpentinization and the inorganic synthesis of H₂ in planetary surfaces. *Icarus* 186:557–561.
5. Lilley MD, et al. (1993) Anomalous CH₄ and NH₄⁺ concentrations at an unsedimented mid-ocean-ridge hydrothermal system. *Nature* 364:45–47.
6. James RH, Elderfield H, Palmer MR (1995) The chemistry of hydrothermal fluids from the Broken Spur site at 29°N Mid-Atlantic Ridge. *Geochim Cosmochim Acta* 59:651–659.
7. Schulte M, Blake D, Hoehler T, McCollom T (2006) Serpentinization and its implications for life on the early Earth and Mars. *Astrobiology* 6:364–376.
8. Charlou JL, Donval JP, Fouquet Y, Jean-Baptiste P, Holm N (2002) Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14' N, MAR). *Chem Geol* 191:345–359.
9. Sherwood Lollar B, Westgate TD, Ward JA, Slater GF, Lacrampe-Couloume G (2002) Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs. *Nature* 416:522–524.
10. Proskurowski G, et al. (2008) Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* 319:604–607.

11. Taran YA, Varley NR, Inguaggiato S, Cienfuegos E (2010) Geochemistry of H₂- and CH₄-enriched hydrothermal fluids of Socorro Island, Revillagigedo Archipelago, Mexico: Evidence for serpentinization and abiogenic methane. *Geofluids* 10:542–555.
12. Bradley AS, Summons RE (2010) Multiple origins of methane at the Lost City Hydrothermal Field. *Earth Planet Sci Lett* 297:34–41.
13. McCollom TM, Seewald JS (2001) A reassessment of the potential for reduction of dissolved CO₂ to hydrocarbons during serpentinization of olivine. *Geochim Cosmochim Acta* 65:3769–3778.
14. Oze C, Sharma M (2005) Have olivine, will gas: Serpentinization and the abiogenic production of methane on Mars. *Geophys Res Lett* 32:L10203.
15. Berndt ME, Allen DE, Seyfried WE (1996) Reduction of CO₂ during serpentinization of olivine at 300 °C and 500 bar. *Geology* 24:351–354.
16. McCollom TM, Seewald JS (2006) Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. *Earth Planet Sci Lett* 243:74–84.
17. Foustoukos DI, Seyfried WE (2004) Hydrocarbons in hydrothermal vent fluids: The role of chromium-bearing catalysts. *Science* 304:1002–1005.
18. Janecky DR, Seyfried WE (1986) Hydrothermal serpentinization of peridotite within the oceanic crust: Experimental investigations of mineralogy and major element chemistry. *Geochim Cosmochim Acta* 50:1357–1378.
19. Horita J, Berndt ME (1999) Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. *Science* 285:1055–1057.
20. Fu Q, Sherwood Lollar B, Horita J, Lacrampe-Couloume G, Seyfried WE (2007) Abiotic formation of hydrocarbons under hydrothermal conditions: Constraints from chemical and isotope data. *Geochim Cosmochim Acta* 71:1982–1998.
21. Evans BW (2010) Lizardite versus antigorite serpentinite: Magnetite, hydrogen, and life(?). *Geology* 38:879–882.
22. Jones LC, Rosenbauer R, Goldsmith JJ, Oze C (2010) Carbonate control of H₂ and CH₄ production in serpentinization systems at elevated P-Ts. *Geophys Res Lett* 37:L14306.
23. Dick HJ, Bullen T (1984) Chromian spinel as a petrogenetic indicator in abyssal and alpine-type peridotites and spatially associated lavas. *Contrib Mineral Petrol* 86:54–76.
24. Oze C, Bird DK, Fendorf SE (2007) Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proc Natl Acad Sci USA* 104:6544–6549.
25. Oze C, Fendorf SE, Bird DK, Coleman R (2004) Chromium geochemistry in serpentinized ultramafic rocks and serpentine soils in the Franciscan Complex of California. *Am J Sci* 304:67–101.
26. Seyfried WE, Pester NJ, Ding K, Rough M (2011) Vent fluid chemistry of the Rainbow hydrothermal system (36 °N, MAR): Phase equilibria and in situ pH controls on subseafloor alteration processes. *Geochim Cosmochim Acta* 75:1574–1593.
27. Kelley DS, et al. (2005) A serpentinite-hosted ecosystem: The Lost City hydrothermal field. *Science* 307:1428–1434.
28. Seewald JS, Zolotov MY, McCollom TM (2006) Experimental investigation of single carbon compounds under hydrothermal conditions. *Geochim Cosmochim Acta* 70:446–460.
29. Charlou JL, et al. (2000) Compared geochemical signatures and the evolution of Menez Gwen (37° 50' N) and Lucky Strike (37° 17' N) hydrothermal fluids, south of the Azores Triple Junction on the Mid-Atlantic Ridge. *Chem Geol* 171:49–75.
30. Schmidt K, Koschinsky A, Garbe-Schonberg D, de Carvalho LM, Seifert R (2007) Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15° N on the Mid-Atlantic Ridge: Temporal and spatial investigation. *Chem Geol* 242:1–21.
31. Mumma MJ, et al. (2009) Strong release of methane on Mars in northern summer 2003. *Science* 323:1041–1045.
32. Ehlmann BL, Mustard JF, Murchie SL (2010) Geologic setting of serpentine deposits on Mars. *Geophys Res Lett* 37:L06201.
33. Krasnopolsky VA, Feldman PD (2001) Detection of molecular hydrogen in the atmosphere of Mars. *Science* 294:1914–1917.
34. Von Damm KL (1990) Seafloor hydrothermal activity: Black smoker chemistry and chimneys. *Annu Rev Earth Planet Sci* 18:173–204.