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H_2/CH_4 Ratios Cannot Reliably Distinguish Abiotic vs. Biotic Methane in Natural Hydrothermal Systems

Susan Q. Lang
University of South Carolina - Columbia, slang@geol.sc.edu

G. L. Früh-Green

D. S. Kelley

M. D. Lilley

G. Proskurowski

See next page for additional authors

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Author(s)
Susan Q. Lang, G. L. Früh-Green, D. S. Kelley, M. D. Lilley, G. Proskurowski, and E. P. Reeves

LETTER

H_2/CH_4 ratios cannot reliably distinguish abiotic vs. biotic methane in natural hydrothermal systems

In their paper, Oze et al. (1) used H_2/CH_4 ratios to assess the origin of methane in serpentinization systems on Earth and Mars, with ratios <33 indicating that "life is likely present and active." The production of CH_4 and H_2 in oceanic and continental hydrothermal systems has been intensively studied for several decades by using numerous techniques (e.g., ^{13}C, ^{14}C, thermodynamic modeling) in conjunction with comprehensive fluid analyses. Based on this body of work, we argue that H_2/CH_4 ratios are inappropriate for determining the origin of methane on this planet and likely on others. Artificially high H_2/CH_4 ratios in benchtop hydrothermal serpentinization experiments do not place realistic constraints on the complex multiple processes affecting CH_4 and H_2 in natural hydrothermal systems, despite their claims.

Of the nine "biotic serpentinization systems" cited (1), eight have temperatures (>150 °C) that argue against biological methanogenesis [Ashadze I and II, Broken Spur, Endeavour, Logatchev, Lucky Strike, Menez Gwen, and Rainbow (2)] and four are hosted in magmatically robust basaltic crust not undergoing serpentinization (Broken Spur, Endeavour, Lucky Strike, and Menez Gwen). Furthermore, thermogenic decomposition of buried sedimentary organic matter is considered the primary source of CH_4 at Endeavour (3), which has the lowest cited H_2/CH_4 ratio (~0.1), and is therefore not directly "biotic." Oze et al. (1) cited Ashadze II as having the highest ratio (~33), serving "as an upper bound for natural systems with dominantly abiogenic CH_4 and minimal biological activity," but fail to include higher H_2/CH_4 ratios (~46) from serpentinite-influenced systems (4), or similarly high values from other basaltic systems in which serpentinization does not influence either volatile. Also, dissolved hydrocarbons at Ashadze II show ^{13}C enrichments with carbon chain length (2) consistent with a thermogenic, not abiotic, origin (5). For the remaining systems, multiple lines of evidence still argue for a dominantly abiotic origin for methane without significant biotic inputs. These include methane $\delta^{13}C$ and $\Delta^{14}C$ signatures, relative concentrations and $\delta^{13}C$ signatures of C_1–C_4 hydrocarbons, a lack of sedimentary inputs, and a lack of clear evidence for significant microbial methanogenesis (2, 5). Minor contributions of magmatically degassed methane are also neglected, yet this is likely the dominant source at Broken Spur (1), where H_2 and CH_4 are low, despite "biotic" ratios according to Oze et al. (1).

Similar to CH_4, H_2 can have multiple sources, as well as sinks, and is more reactive. High-temperature reactions with mineral assemblages (aside from serpentinization), microbial oxidation, and sulfate reduction can influence H_2 production or consumption, and therefore H_2/CH_4 ratios, without impacting CH_4. Additionally, H_2 production by serpentinization of olivine-rich igneous rock is highly complex, and can vary over a wide range of conditions in nature that are often highly simplified in hydrothermal experiments. It is therefore unreasonable to apply purely experimental H_2/CH_4 ratios to diverse natural hydrothermal systems. The distinction made by Oze et al. (1) between "biotic serpentinization systems" and "abiotic serpentinization experiments" is instead better explained as a difference between the complexity of natural systems and the inability to replicate them with simple benchtop experiments.

Susan Q. Lang[a,1], Gretchen L. Früh-Green[a], Deborah S. Kelley[b], Marvin D. Lilley[b], Giora Proskurowski[b], and Eoghan P. Reeves[c]
[a]Department of Earth Sciences, Eidgenössische Technische Hochschule Zürich, 8092 Zürich, Switzerland; [b]School of Oceanography, University of Washington, Seattle, WA 98195; and [c]MARUM Center for Marine Environmental Sciences, University of Bremen, 28359 Bremen, Germany

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[1]To whom correspondence should be addressed. E-mail: susan.lang@erdw.ethz.ch.

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