PNAS LETTER

Reply to Schoell: Implications of a temperature trend in methane evolved from Cumberland during Mars evolved gas analyses experiments

Christopher H. House[a,b,1], Heather B. Franz[c], Gregory M. Wong[a,b], Paul R. Mahaffy[c], Alexander Pavlov[c], Andrew Steele[d], Sushil Atreya[e], and Charles A. Malespin[c]

In response to our reporting the carbon isotopic compositions of CH_4 released during pyrolysis of solid Mars sediments (1), Schoell (2) states that our full dataset does not follow a trend with temperature observed for the pyrolysis of Earth kerogen-rich sediments. We appreciate Schoell's highlighting that the changing isotopic composition is an important constraint useful for understanding the origin of CH_4 released during pyrolysis. Our published dataset (1) includes analyses of five aliquots from the Cumberland drill hole, one of the locations where highly ^{13}C-depleted carbon was observed by the tunable laser spectrometer (TLS). A different temperature cut was sent to TLS for each aliquot, but, collectively, CH_4 released from Cumberland during pyrolysis follows a trend with temperature similar to that observed in the West Siberian hydrocarbon source rocks (3) mentioned in Schoell's (2) critique, once the terrestrial data are adjusted to reflect a more ^{13}C-depleted source carbon (Fig. 1). The other samples shown in Fig. 1, single aliquots from multiple other drill holes, are interpreted to have similar carbon isotopic values for their CH_4 sources. These samples, when taken together, also show a trend with temperature similar to that observed during pyrolysis of kerogen-rich rocks on Earth.

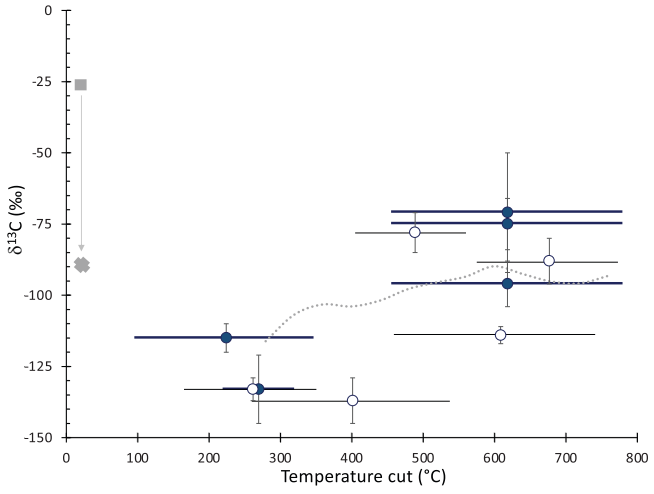

Fig. 1. TLS CH_4 $\delta^{13}C$ results (±1 SE) from evolved gas analyses of samples of the Cumberland drill hole material (filled circles) as a function of the temperature cut used for TLS (1). Horizontal lines show the complete range of each temperature cut. The gray dashed curve represents the experimental results reported in ref. 3 but adjusted to approximate the isotopic values for methane released from the Cumberland samples. To generate such strong depletions under this scenario, the original $\delta^{13}C$ value for the Cumberland carbon source would need to be approximately −90‰ (gray cross); the gray square shows, for reference, the $\delta^{13}C$ of the West Siberian hydrocarbon source rocks studied in ref. 3. The open circles are other Gale crater CH_4 TLS isotope results (GB2, HF, RH, HU, and EB) that, while each from separate experiments, were interpreted to have evolved CH_4 $\delta^{13}C$ values in family with the Cumberland set, due to the strong ^{13}C depletions observed.

Notably, unlike West Siberia's hydrocarbon source rocks, the Gale crater samples represent multiple geologic assemblages (Yellowknife Bay clastic sediments, mudstone-rich Murray lacustrine sediments, Vera Rubin ridge geochemically altered sediments, sandstone-rich Carolyn Shoemaker sediments, and the Stimson sandstone deposited after a disconformity). The observed geologies (including geochemical alteration, veining, and an erosional disconformity) imply that our full suite of samples represents significant geological time, so it is not surprising that *Curiosity*'s 25-km traverse encountered a variety of organics with differing isotopic compositions. Additionally, the Gale crater samples release mineral-bound carbon at a variety of temperatures (4), indicating that the full dataset reported includes pyrolysis CH_4 released from a variety of different carbon sources, as previously discussed (1).

Schoell (2) ends his critique with a claim that our paper "infer[s] methane as a proven biosignature on Mars." We do not. Our report exhaustively discusses mechanisms (abiotic and biotic) by which isotopic fractionations can occur [including serpentinization (5, 6)] and how these processes could apply to Gale crater sediments (1). The discussion narrows the options to a few working hypotheses, each requiring further exploration before being confirmed or refuted. Naturally, one hypothesis invokes large carbon isotopic fractionations mediated by methanogens under certain conditions (7), which result in ^{13}C-depleted subsurface CH_4 on Earth (8). The other working hypotheses utilize large isotopic fractionations observed between CO and dust in interstellar giant molecular clouds or suspected for UV-mediated CO_2 reduction in the Martian atmosphere (1). By presenting distinct working hypotheses, we intentionally aimed to remain cautious about biosignature implications of the most ^{13}C-depleted values and provide the community with optimistic guidance as to how progress can be made in understanding the origin of the specific carbon we reported.

Author affiliations: [a]Department of Geosciences, The Pennsylvania State University, University Park, PA 16802; [b]Earth and Environmental Systems Institute, The Pennsylvania State University, University Park, PA 16802; [c]Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD 20771; [d]Earth and Planets Laboratory, Carnegie Institution for Science, Washington, DC 20015; and [e]Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI 48109

Author contributions: C.H.H. performed research; C.H.H. analyzed data; and C.H.H., H.B.F., G.M.W., P.R.M., A.P., A.S., S.A., and C.A.M. wrote the paper.

The authors declare no competing interest.

[1]To whom correspondence may be addressed. Email: chrishouse@psu.edu.

Published July 11, 2021.

1. C. H. House, G. M. Wong, C. R. Webster, P. R. Mahaffy, Depleted carbon isotope compositions observed at Gale crater, Mars. *Proc. Natl. Acad. Sci. U.S.A.* **119**, e2115651119 (2022).
2. M. Schoell, Methane $^{13}C/^{12}C$ isotope analyses with the SAM-EGA pyrolysis instrument suite on Mars *Curiosity* rover: A critical assessment. *Proc. Natl. Acad. Sci. U.S.A.*, 10.1073/pnas.2205344119 (2022).
3. B. Cramer, B. M. Krooss, R. Littke. Modelling isotope fractionation during primary cracking of natural gas: A reaction kinetic approach. *Chem Geol.* **149**, 235–250 (1998).
4. B. Sutter *et al.*, Evolved gas analyses of sedimentary rocks and eolian sediment in Gale Crater, Mars: Results of the Curiosity rover's sample analysis at Mars instrument from Yellowknife Bay to the Namib Dune. *J. Geophys. Res. Planets* **122**, 2574–2609 (2017).
5. G. Etiope, B. L. Ehlmann, M. Schoell, Low temperature production and exhalation of methane from serpentinized rocks on Earth: A potential analog for methane production on Mars. *Icarus* **224**, 276–285 (2013).
6. A. Steele *et al.*, Organic synthesis associated with serpentinization and carbonation on early Mars. *Science* **375**, 172–177 (2022).
7. T. Okumura *et al.*, Hydrogen and carbon isotope systematics in hydrogenotrophic methanogenesis under H_2-limited and H_2-enriched conditions: Implications for the origin of methane and its isotopic diagnosis. *Prog. Earth Planet. Sci.* **3**, 14 (2016).
8. M. Schoell, Multiple origins of methane in the Earth. *Chem. Geol.* **71**, 1–10 (1988).