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Biosignatures and abiotic constraints on early life

Arising from: Y. Ueno, K. Yamada, N. Yoshida, S. Maruyama & Y. Isozaki *Nature* 440, 516–519 (2006)

Ueno *et al.*¹ contend that methane found in fluid inclusions within hydrothermally precipitated quartz in the Dresser Formation of western Australia (which is roughly 3.5 Gyr old) provides evidence for microbial methanogenesis in the early Archaean era. The authors discount alternative origins for this methane, suggesting that the range of $\delta^{13}\text{C}_{\text{CH}_4}$ values that they record (–56 to –36‰) is attributable to mixing between a primary microbial end-member with a $\delta^{13}\text{C}_{\text{CH}_4}$ value of less than –56‰ and a mature thermogenic gas enriched in ^{13}C (about –36‰). However, abiotic methane produced experimentally^{2,3} and in other Precambrian greenstone settings^{4,5} has ^{13}C -depleted $\delta^{13}\text{C}_{\text{CH}_4}$ values, as well as $\Delta^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ relationships that encompass the range measured for the inclusions by Ueno *et al.* — which suggests that an alternative, abiotic origin for the methane is equally plausible. The conclusions of Ueno *et al.* about the timing of the onset of microbial methanogenesis might not therefore be justified.

The range of isotopic values for abiotic methane shown in Fig. 2c of Ueno *et al.*¹ differs distinctly from those from thermogenic and microbial sources, and does not encompass the methane in their fluid inclusions. However, the range of $\delta^{13}\text{C}_{\text{CH}_4}$ for abiotic hydrocarbons is larger than that used in their comparison. Abiotic methane end-members in Precambrian Shield rocks extend to much lighter $\delta^{13}\text{C}_{\text{CH}_4}$ values (–47 to –28‰)^{4,5}. Also, as noted by Ueno *et al.*, experimental studies² indicate that abiotic synthesis using a Ni–Fe alloy catalyst may produce methane with a range of isotopic compositions ($\delta^{13}\text{C}_{\text{CH}_4}$ values of –54 to –19‰ at 200–300 °C) that is similar to the range in the inclusions¹. Although those

results have not been duplicated², they have not been disputed either. In fact, hydrothermal abiotic methane synthesis has been confirmed with Ni–Fe alloy⁶ and other potential mineral catalysts^{7,8}.

The values of $\Delta^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ measured by Ueno *et al.* in their inclusions (34–52‰; see their Supplementary Table 2) span a range that is identical to, or even smaller than, those produced in abiotic synthesis experiments (33–66‰)^{2,3}. Furthermore, the experimental range would encompass the larger value the authors infer for primary inclusions ($\Delta^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$ >52‰). The authors also contend that the lack of C_2^+ compounds in those inclusions is in agreement with a microbial origin; however, C_2^+ hydrocarbons were not detected during methane synthesis in abiotic experiments² either, so such reactions can also produce methane with a low $\text{C}_2^+ / (\text{C}_1 + \text{C}_2^+)$ ratio (<<0.01). Therefore, neither an absence of C_2^+ nor isotopic compositions can distinguish between microbial and abiotic origins for this data set, even when both factors are considered together.

Ueno *et al.* also discount an abiotic source on the grounds that Fe–Ni alloys and other catalysts for Fischer–Tropsch-type synthesis reactions would not have existed in the surrounding rocks at conditions prevailing during silica precipitation. But abiotic methane could have been synthesized during interaction of migrating hydrothermal fluids with ultramafic rocks elsewhere in the system in the presence of either Ni–Fe alloy or other mineral catalysts, and transported to the site of quartz deposition^{3,9,10}, so the absence of suitable catalysts immediately adjacent to the fluid inclusion-bearing quartz would not preclude an abiotic origin. Indeed, Ueno *et al.* explain the

inferred thermogenic origin of methane in the secondary inclusions using migration from surrounding rocks.

The key criteria used by Ueno *et al.* to establish a microbial origin for methane in the inclusions from the Dresser Formation are therefore equally consistent with an abiotic origin, and their conclusion about the antiquity of the onset of microbial methanogenesis should be viewed with caution. Biosignatures that are mimicked by abiotic processes need to be analysed closely to evaluate not only signs of life in rocks from the early Earth but also the search for life on other planets.

Barbara Sherwood Lollar*,

Thomas M. McCollom†

*Department of Geology, University of Toronto, Toronto, Ontario M5S 3B1, Canada

e-mail: bslollar@chem.utoronto.ca

†Center for Astrobiology and Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colorado 80309, USA

1. Ueno, Y., Yamada, K., Yoshida, N., Maruyama, S. & Isozaki, Y. *Nature* 440, 516–519 (2006).
2. Horita, J. & Berndt, M. E. *Science* 285, 1055–1057 (1999).
3. McCollom, T. M. & Seewald, J. S. *Earth Planet. Sci. Lett.* 243, 74–84 (2006).
4. Sherwood Lollar, B., Westgate, T. D., Ward, J. A., Slater, G. F. & Lacrampe-Couloume, G. *Nature* 416, 522–524 (2002).
5. Sherwood Lollar, B. *et al.* *Chem. Geol.* 226, 328–339 (2006).
6. McCollom, T. M. & Seewald, J. S. *Geochim. Cosmochim. Acta* 67, 3625–3644 (2003).
7. McCollom, T. M. & Seewald, J. S. *Geochim. Cosmochim. Acta* 65, 3769–3778 (2001).
8. Foustoukos, D. I. & Seyfried, W. E. *Jr Science* 304, 1002–1005 (2004).
9. Brasier, M. D. *et al.* *Precamb. Res.* 140, 55–102 (2005).
10. Lindsay, J. F. *et al.* *Precamb. Res.* 143, 1–22 (2005).

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Ueno *et al.* reply

Replying to: B. Sherwood Lollar & T. M. McCollom *Nature* 444, doi: 10.1038/nature05499 (2006)

Sherwood Lollar and McCollom¹ suggest that abiotic reactions, in particular those catalysed by Fe–Ni alloys, might be responsible for the methane recorded in our fluid inclusions². They point out that ^{13}C in methane that is produced abiotically can be substantially depleted under field and laboratory conditions. However, native metal catalysis would not only have been implausible in the sulphidic environment of the basalt-hosted Dresser

hydrothermal system, but it would also have been inconsistent with the isotopic fractionation between CH_4 and CO_2 that we note in the primary fluid².

Sherwood Lollar and McCollom¹ overlook the petrography of the fluid inclusions, which shows that the $\delta^{13}\text{C}$ value of the primary methane should be less than –56‰ (ref. 2). However, this value is a maximum estimate of the fluid inclusion's $\delta^{13}\text{C}_{\text{CH}_4}$ value, because primary

methane would have been mixed with ^{13}C -enriched secondary methane². The isotopic fractionation between primary CH_4 and CO_2 should therefore be greater than 52‰.

Fischer–Tropsch-type reactions catalysed by Fe–Ni alloy at 200–300 °C (refs 3, 4) might produce methane depleted of ^{13}C by 30–50‰ relative to CO_2 ; even more isotopic fractionation between CH_4 and CO_2 is achieved at lower temperatures³. However, Fe