

Fractionation of carbon isotopes in *Methanosarcina barkeri*

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SUMMONS¹

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The ¹³C content of the organic constituents and products of an organism are controlled by the ¹³C content of the growth substrate, the growth rate or degree of substrate utilization, the relative flux of carbon through various parts of the biochemical network, and the isotopic fractionation imposed by the enzymes of that network [1].

Methane is an important part of the Earth's carbon cycle, not least because of its role as a greenhouse gas. Despite this, there is little quantitative understanding of the various methane sources to the atmosphere and hydrosphere. These sources may include abiotic CO₂ reduction, thermogenic cracking of hydrocarbons, microbial production by Euryarchaeota, and direct CH₄ emissions by terrestrial plants [2]. Methane sources are often attributed on little more than δ¹³C values. However, the multitude of controls on ¹³C fractionation suggests that this approach is flawed.

We sought to examine the variability of the ¹³C content of the products of methanogens, including biomass, methane, and lipids (archaeol and *sn*-2 hydroxyarchaeol), as a function of growth substrate and rate. We chose *Methanosarcina barkeri* because of its ability to utilise various substrates and grew pure cultures on CO₂/H₂, acetate, trimethylamine, and methanol.

Growth without substrate limitation yielded a range of ¹³C discrimination factors, with growth on methanol yielding methane, biomass and lipids most depleted in ¹³C relative to substrate (77.6‰, 30.5‰, and 50.0‰ respectively) and growth on acetate yielding products least depleted (35‰, 4.6‰, and 5.7‰). Substrate-limited growth afforded smaller depletions in ¹³C on all substrates.

The compilation of these results allows us to better understand fractionation factors imposed by the various enzymes utilized in growth on different substrates. It also suggests that biological fraction of carbon in methane production can not be generalized to the common inference that biological methane has δ¹³C < -50‰. Carbon isotope fractionations imposed by methanogenic archaea can vary as strongly as those imposed by photoautotrophs, and under substrate-limiting conditions biological methane may be surprisingly enriched in ¹³C.

References

- [1] Hayes, J.M. (2001) *Reviews in Mineralogy & Geochemistry* **42**, 225-227.
- [2] Keppler, F., Hamilton, J.T., Brass, M., and Rockmann, T. (2006) *Nature* **439**, 187-191.