Microbial cycling of hydrocarbons revealed by new isotope tracers

*Alexis Gilbert[1,2], Thomas Giunta[3], Florin Musat[4], Barbara Sherwood-Lollar[3], Keita Yamada[5], Naohiro Yoshida[5,2], Yuichiro Ueno[1,2]

1. Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Japan, 2. Earth-Life Science Institute, Tokyo Institute of Technology, Japan, 3. Department of Earth Sciences, University of Toronto, Canada, 4. Department of Isotope Biogeochemistry Helmholtz-Zentrum für Umweltforschung, Leipzig, Germany, 5. Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, Yokohama, Japan.

Hydrocarbons in natural gas provide insights into potential gas and petroleum accumulations and subsurface biosphere. Stable isotopes (^{2}H, ^{13}C) have been used in the past decades in order to reveal the origin of hydrocarbons, including the potential microbial production and consumption, providing a unique window to the subsurface biosphere [1]. In the past few years, new isotopic tracers have emerged, namely intramolecular isotope analyses. These approaches include multi-substituted species (“clumped” isotopes) [2] and position-specific isotope analysis [3]. Both have the potential to provide unique information regarding the processes and conditions of formation of hydrocarbons.

Here, we present new data on position-specific isotope analysis of propane from sedimentary basins in North America (Michigan basin and Southern Ontario), where economic reservoirs of hydrocarbons accumulate [4]. We use a method we recently developed allowing the determination of d^{13}C values of terminal (CH_3) and central (CH_2) position of propane with a precision of 1‰ [3]. The δ^{13}C value of the central position of propane increases by around 10‰ with increasing bulk δ^{13}C of propane, while the δ^{13}C value of the terminal position is uniform for all the samples measured. The results are not consistent with production models for thermogenic natural gas generation [5], nor with experimental results obtained from thermogenic propane generation. However, the results are consistent with the proposed mechanism for anaerobic bacterial oxidation of propane [6].

When propane is biodegraded by BuS5 –a sulfate-reducing anaerobic bacteria that uses propane as a carbon source [6]– the remaining propane is relatively ^{13}C-enriched in the central position. The position-specific fractionation factor measured for the bacteria is consistent with that observed for canadian natural gas samples, suggesting anaerobic bacterial propane oxidation occurs in the basin. In addition, data from the Michigan basin suggests that anaerobic C_3/C_4 bacterial oxidation is coupled to the production of ethane. Whether the production is biological or not remains to be elucidated.

Overall, the data suggests that position-scpeific isotope composition can help refine the origins of hydrocarbons, in particular microbial production and consumption.

[1] Simkus *et al.* (2016) *Geochimica et Cosmochimica Acta* **173**, 264–283 [2] Stolper *et al.* (2014) *Science* **344**, 1500-1503 [3] Gilbert *et al.* (2016) *Geochimica et Cosmochimica Acta* **177**, 205–216; Suda *et al.* (2017) *GCA* **206**, 201–215 [4] Sherwood Lollar *et al.* (1994) *Bulletin of Canadian Petroleum Geology* **42**, 283–295 [5] Chung *et al.* (1988) *Chem. Geol.* **71**, 97–104; Tang *et al.* (2000) *GCA* **64**, 2673–2687 [6] Jaekel *et al.* (2014) *Environ. Microb.* **16**, 130–140

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