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# Alkylotrophic methanogenesis forms biogenic methane with $\delta^{13}C$ values comparable to thermogenic gas

**LING LI**[1,2], QUAN YUAN[3], JIANG LI[1], YUEYI HUANG[1], YONGGE SUN[4], HAIPING HUANG[5], WENYI GAO[1], JIALAI ZHONG[1], LIN FU[1], WEIDONG WANG[6], JUN ZHANG[7], GILLES COLINET[2], GUNTER WEGENER[8], LEI CHENG[1] AND YAHAI LU[9]

[1]Key Laboratory of Development and Application of Rural Renewable Energy, Chengdu Biogas Institute, Ministry of Agriculture and Rural Affairs
[2]Gembloux Agro Bio Tech, University of Liège
[3]Institute of Geochemistry Chinese Academy of Sciences
[4]Organic Geochemistry Unit, School of Earth Sciences, Zhejiang University
[5]Petroleum Reservoir Group (PRG), Department of Geoscience, Unversity of Calgary
[6]Key Laboratory of Microbial Enhanced Oil Recovery, SINOPEC
[7]Science and Technology Management Department of Shengli Oilfield Company, China Petroleum & Chemical Corporation
[8]MARUM, Center for Marine Environmental Sciences, University of Bremen
[9]College of Urban and Environmental Sciences, Peking University

Methane, a primary component of natural gas, is mainly derived from biogenic and thermogenic origins. Biogenic methane exhibits lower $\delta^{13}C$-$CH_4$(<-55‰)[1, 2] than thermogenic methane. However, secondary microbial methane (SMM), an important biogenic gas formed through the methanogenic degradation of petroleum, was speculated to have $\delta^{13}C$-$CH_4$ from -55‰ to -35‰ [3] overlapping with thermogenic. Conventional methanogenetic pathways cannot adequately explain this deviation, indicating alternative methanogenesis producing methane with less $^{13}C$ depletion. Alkylotrophic methanogenesis differs from previous methanogenic metabolism and is widespread in oil reservoirs [4, 5]. Therefore, we incubated the enrichment culture of alkylotrophic methanogens with the eicosane and several crude oils as substrates ($\delta^{13}C$-values from -35 to -27‰). The accumulated $CH_4$ exhibited $\delta^{13}C$ values of −48‰ to −41‰, $CO_2$ from −7‰ to +14‰. It exhibited smaller carbon isotopic fractionation than other pathways, ranging from -10 to -17‰. Since about 1/3 of methane derives from $CO_2$ reduction, the only likely process with substantial fractionation, the overall fractionation of alkylotrophic methanogenesis will be rather low. Its $\delta^{13}C$ values depart from canonical methanogenesis and plots in the interface between thermogenic and SMM. Given the prevalence of alkylotrophic methanogenesis in subsurface reservoirs, biogenic methane in reservoirs has been previously underestimated. This oversight not only calls for re-evaluating methane inventories in reservoir systems but also implies that subsurface microbial processes could be a more critical component of the global carbon cycle than previously recognized.

**References**

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