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Rita Susilawati, Suzanne D. Golding, Kim A. Baublys, Joan S. Esterle, Stephanie K. Hamilton

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CARBON AND HYDROGEN ISOTOPE FRACTIONATION DURING METHANOGENESIS: A LABORATORY STUDY USING COAL AND FORMATION WATER

Rita Susilawati[a,b*], Suzanne D. Golding[a], Kim A. Baublys[a], Joan S. Esterle[a] and Stephanie K. Hamilton[a]

[a]*School of Earth Sciences, The University of Queensland, St Lucia, Queensland 4072 Australia;*
[b]*Geological Agency of Indonesia, Jl. Sukarno Hatta no 444, Bandung, West Java 40254, Indonesia.*

ABSTRACT

Carbon and hydrogen isotope compositions of CH_4 generated via methanogenesis in cultures of South Sumatra Basin (SSB) coalbed methane (CBM) formation waters grown on coal, acetate and H_2+CO_2 were investigated. CH_4 production and molecular analysis confirmed the presence of active microbial communities that are able to convert coal into CH_4 using both acetoclastic and hydrogenotrophic pathways. The representative bacterial sequences were dominated by *Bacteroidetes*, *Firmicutes* and *Deltaproteobacteria*, while *Methanosaeta* and *Methanosarcina* were the most prevalent archaeal methanogens present in the cultures.

CH_4 produced in this study's culturing experiments has $\delta^{13}C$ values in the range of –50 ‰ to –20 ‰, with most values falling outside the current understanding of the carbon isotopic boundaries for biogenic CH_4 (–110 ‰ to –30 ‰). However, the corresponding apparent carbon isotopic α factor (α_c = 1.02±0.006), and isotopic effect (ε_c = –20.1 ‰ ±15.3) showed that CH_4 in SSB cultures was predominantly produced by acetoclastic methanogenesis, which is consistent with the results of molecular DNA analysis. In addition, the calculated contribution of CO_2 reduction from the $\delta^{13}C$ values of coal-treated cultures was overall < 50 %, further confirming the high contribution of the acetoclastic pathway to CH_4 production in the SSB cultures. The outcome of this experimental study also suggests that $\delta^{2}H$-CH_4 values may not provide a reliable basis for distinguishing methanogenic pathways, while apparent carbon isotopic fractionation factor (α_c) and isotope effect (ε_c) are considered more useful indicators of the methanogenic pathway.

The high $\delta^{13}C$-CH_4 values (>–30 ‰) and the dominance of *Methanosaeta* over *Methanosarcina* indicate that methanogens within the SSB cultures were operating at low substrate concentrations. An unusually positive $\delta^{13}C$-CH_4 suggests a substrate depletion effect, which is thought to be related to a decrease in the relative abundance of key bacterial coal degraders with formation water inoculum storage time. Closer observation of $\delta^{13}C$-CH_4 values during the growth of cultures within a single experiment also showed a ^{13}C-enrichment trend over time. At log phase of growth, the CH_4 produced was ^{13}C-depleted when compared to the stationary phase that also indicates substrate depletion effects. Finally, the $\delta^{13}C$-CH_4 values encountered in this study (as high as –20 ‰) highlight the possible positive extension of $\delta^{13}C$-CH_4 values of acetoclastic methanogenesis from those currently reported in the literature for natural and experimental samples (as high as –30 ‰).

Keywords: Biogenic gas, coal, culture experiment, isotopic composition