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Isotopic characterization of abiotic methane in hydrothermal systems: An experimental study

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To better understand the formation of abiotic methane in subseafloor hydrothermal systems, a series of laboratory experiments was performed. Dissolved carbon dioxide and hydrogen gases were introduced into a flow-through reactor with presence of a mineral catalyst (magnetite or bunsenite), analogous to a thermodynamically open system. The experiments were conducted at temperatures ranging from 150 to 300 °C and pressures up to 300 bars.

Methane was the predominant dissolved gas product, with less amount of ethane and propane generated in experiments. The carbon isotopic composition of CH_4 is more depleted in ^{13}C than the starting CO_2, which has a $\delta^{13}C$ value of –38.2‰. At 150 °C, the carbon isotope value of CH_4 is –82.5‰ and –80.6‰ after 24 and 200 hours of reaction, respectively, showing a trend of increase with time. The $\delta^{13}C$ value of dissolved CO_2 is –37.2‰ and –35.4‰ in the same time span. The fractionation factor between CO_2 and CH_4, $10^3\ln\alpha(CO_2\text{-}CH_4)$, is high than the equilibrium value (41.0) at 150 °C. The $\delta^{13}C$ value of C_2H_6 is lower than CH_4, –85.0‰ and –83.5‰, respectively. There is an "isotope reversal" of $\delta^{13}C$ values for CH_4 and C_2H_6, as observed in light alkanes of abiotic origin in geological environments. No carbon isotopic equilibrium between any pair of carbon-bearing compounds (dissolved CO_2, CH_4, and C_2H_6) has been reached at experimental temperatures, confirming the kinetic nature of abiotic hydrocarbon formation processes.

The variation of the hydrogen isotope value of CH_4 with reaction time is much subtle. The δD value of CH_4 varies from –518.5‰ to –519.9‰ at 150 °C, with the average value of –519.1‰. There is an apparent positive relationship between the δD value of CH_4 and temperature. The average δD value of CH_4 increases from –519.1‰ at 150 °C to –405.5‰ at 300 °C.

The clumped isotope measurement ($\delta^{13}CH_3D$) of methane, which is currently in progress, may put more constraints on the formation of abiotic methane. Combined with generation kinetic data, those results would facilitate our understanding of the reaction mechanism of abiotic methane formation in hydrothermal systems and its contribution to the overall carbon cycle on Earth.