Experimental study of generation kinetics for abiotic methane in hydrothermal systems

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To better understand methane formation by Fischer-Tropsch type synthesis in subseafloor hydrothermal systems, a series of experiments were conducted with a flow-through reactor. The advantage of using this setup is each potential controlling factor can be maintained constant in a thermodynamically open system, facilitating assessment of its individual effect on methane generation, kinetics in particular.

The carbon precursor in the experiments is CO_2, while magnetite is the mineral catalyst. Experimental results have shown that several environmental variables control methane formation, including temperature, residence time of fluids (flow rate), and redox condition ($H_{2(aq)}/CO_{2(aq)}$ ratio). The methane concentration increases under conditions with lower temperatures, longer fluid residence times, or higher reducing levels. For example, at 250 °C and fluid flow rate of 0.50 ml/min, methane becomes present only when the $H_{2(aq)}/CO_{2(aq)}$ ratio is above 2. The methane concentration reaches 0.3 µmol/kg when the $H_{2(aq)}/CO_{2(aq)}$ ratio is 5, and becomes 1.6 µmol/kg when the flow rate decreases from 0.50 to 0.15 ml/min. The same trend is also observed at 300 °C. However, the methane concentration is always lower than the value at 250 °C under otherwise similar conditions.

The overall formation rate of methane is 4.0×10^{-11} mol/kg·s at 250 °C, and 1.5×10^{-11} mol/kg·s at 300 °C. They are different than the values previously reported for the Fischer-Tropsch synthesis in gas phases. There are two possible reasons attributing to the slow formation kinetics of methane in this study. One is energy barrier induced by high water pressure for adsorption of H_2 and CO_2 (or CO) onto catalyst surfaces and subsequent desorption of CH_4. The other is different organic intermediary and/or different rate-determining reaction under hydrothermal conditions than in gas phases.

Therefore, quantitative identificatin of organic intermediary, currently in progress, is essential to elucidating intrinsic controlling factors of abiotic methane formation and its time scale. The kinetics study would advance our understanding of organic synthesis in submarine hydrothermal systems on Earth, and other planetary bodies.